SIMULATION OF A MIXER - SETTLER

LIQUID EXTRACTION COLUMN

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By

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SCOPE AND CONTENTS: Lagrangian interpolation and the Fibonacci
search scheme were used in the steady - state simulation of a
Scheibel extraction column on the IBM 7040 computer. The first
technique allowed easy representation of graphical data in a form
suitable for the digital computer while the second provided a
powerful sequential search plan to carry out the trial and error
material balance calculation. The features of equilibrium and non-
equilibrium models which utilized the above techniques are discussed
and compared.

The non-equilibrium model was also used to calculate the
transient response which was then compared with experimental results.
The Runge-Kutta-Gill process was used to integrate the transient
equations while Lagrangian interpolation was used to remove the
restriction of a linear equilibrium relationship.

Steady - state and transient experimental results used in the
above calculations were obtained from the Scheibel extraction column
in the Operations Laboratory.

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I INTRODUCTION

1.1 General

As the use of computers in the evaluation and control of chemical operations advances, the need for mathematical models which will accurately simulate these processes becomes essential. In order to achieve a complete model which will predict the transient as well as the steady - state characteristics, much preliminary work must first be completed.

This report presents an approach to the problems of data representation and calculational procedures concerning liquid - liquid extraction. Methods of transforming graphical information into analytic forms suitable for computation have been tested on two steady-state models. These steady - state representations of a Scheibel extraction column involved both equilibrium and non-equilibrium stages and produced valuable information for subsequent transient models.

These transient models, by using the techniques developed for the steady - state simulation, have allowed prediction of the concentration response curves. These curves have subsequently been compared to those obtained experimentally and the congruency used as the criterion of model adequacy.

1.2 Data Representation

In general, equilibrium concentrations for three component, two phase systems have been represented graphically. From these plots empirical equations or least - square fits have been developed to represent the data analytically.

Hand (1) proposed the first empirical plots and equations for solute distribution. The equation derived relates the concentration of the solute in the solvent - rich or extract phase to the concentration in the solvent - lean or raffinate phase:

$$EC/EB = k \ (RC/RA)^m \qquad (1)$$

where E represents the extract phase, R the raffinate phase, C the concentration of solute, A the concentration of diluent and B the concentration of solvent. By plotting EC/EB versus RC/RA on log - log graph paper a straight line with slope m and intercept k should result if the system is well behaved.

Brancker, Hunter and Nash (2) in a later paper attempted to reduce tie line concentration relationships to straight lines by using a special weight percentage scale. These authors also found that by plotting weight percentages of the two nonconsolute liquids on rectangular coordinates the binodal curve could be approximated by a rectangular hyperbola. Using this last information, Bachman (3) subsequently obtained the following equation for the equilibria:

$$RA = b + a \ (RA/EB) \qquad (2)$$

where a and b are arbitrary constants which depend upon the particular system. Equation (2) indicates that a plot of RA versus the ratio RA/EB will produce a linear relationship.

Othmer and Tobias (4), starting from the Bachman equation, were able to reduce it by suitable algebraic manipulations to equation (3):

$$\log \left(\frac{100 - RA)}{RA}\right) = \log \left(\frac{100 - EA}{EA}\right) + \text{constant} \tag{3}$$

Providing the system used is not exceptional, this equation again represents a linear relationship. Equation (3) thus reduces the Bachman plots with different slopes to straight line plots with the same slope of unity. For systems with partially miscible nonconsolute liquids this last equation can be modified to include an additional parameter, n, whose value will depend upon the extent of miscibility:

$$\log \left(\frac{100 - RA}{RA}\right) = n \log \left(\frac{100 - EA}{EA}\right) + \text{constant} \tag{4}$$

The presence of the nonunity slope may be due to the formation of either associated or dissociated molecules in solution.

However, as Treybal (5) illustrates, these procedures lack generality. For each new system the specific constants must be evaluated in order to obtain an analytical representation of the equilibrium data.

1.3 Equilibrium Stage Calculation

A theoretical or equilibrium stage can be defined as a contacting device in which material is transferred so efficiently that the leaving streams may be considered to be in equilibrium with each other.

For liquid extraction, the calculation of the number of theoretical stages on a ternary solubility diagram involves an overall material balance, a set of individual stage balances, and the determination

of equilibrium concentrations from tie lines.

Consider Figure 1 in which the flow rate and concentrations of the feed F, solvent S, extract E_1, and raffinate R_N are known. Equation (5) represents the overall balance while equation (6) formulates the stage balance:

$$F + S = E_1 + R_N \tag{5}$$

$$F + E_{J+1} = E_1 + R_J \tag{6}$$

Rearranging equation (5):

$$F - E_1 = R_N - S = 0 \tag{7}$$

where O is the operating point. From equation (6) it is apparent that the operating point will also occur at the intersection of the lines through $E_1 F$ and $E_{J+1} R_J$ as shown in Figure 2.

The calculation proceeds as follows: first, the overall material balance locates the operating point O; secondly, the tie line through E_1 fixes the point R_1; thirdly, the stage balance using F, E_1 and R_1 establishes E_2. Repeated application of this sequence eventually locates R_J below R_N. The number of steps required to proceed from E_1 to R_N then represents the number of equilibrium stages.

1.4 Non-Equilibrium Stage Calculation

The concept of the equilibrium stage has been a valuable tool for the analysis and design of the steady - state behaviour of process equipment. However, it is less useful for models of processes which are transient in nature. In this study a comparison of the concept of
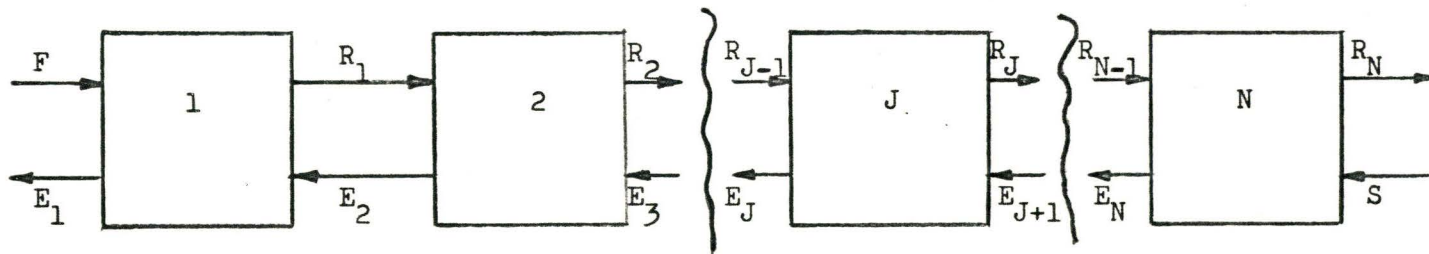
FIGURE 1: STAGEWISE EXTRACTION

FIGURE 2: EQUILIBRIUM STAGE CALCULATION
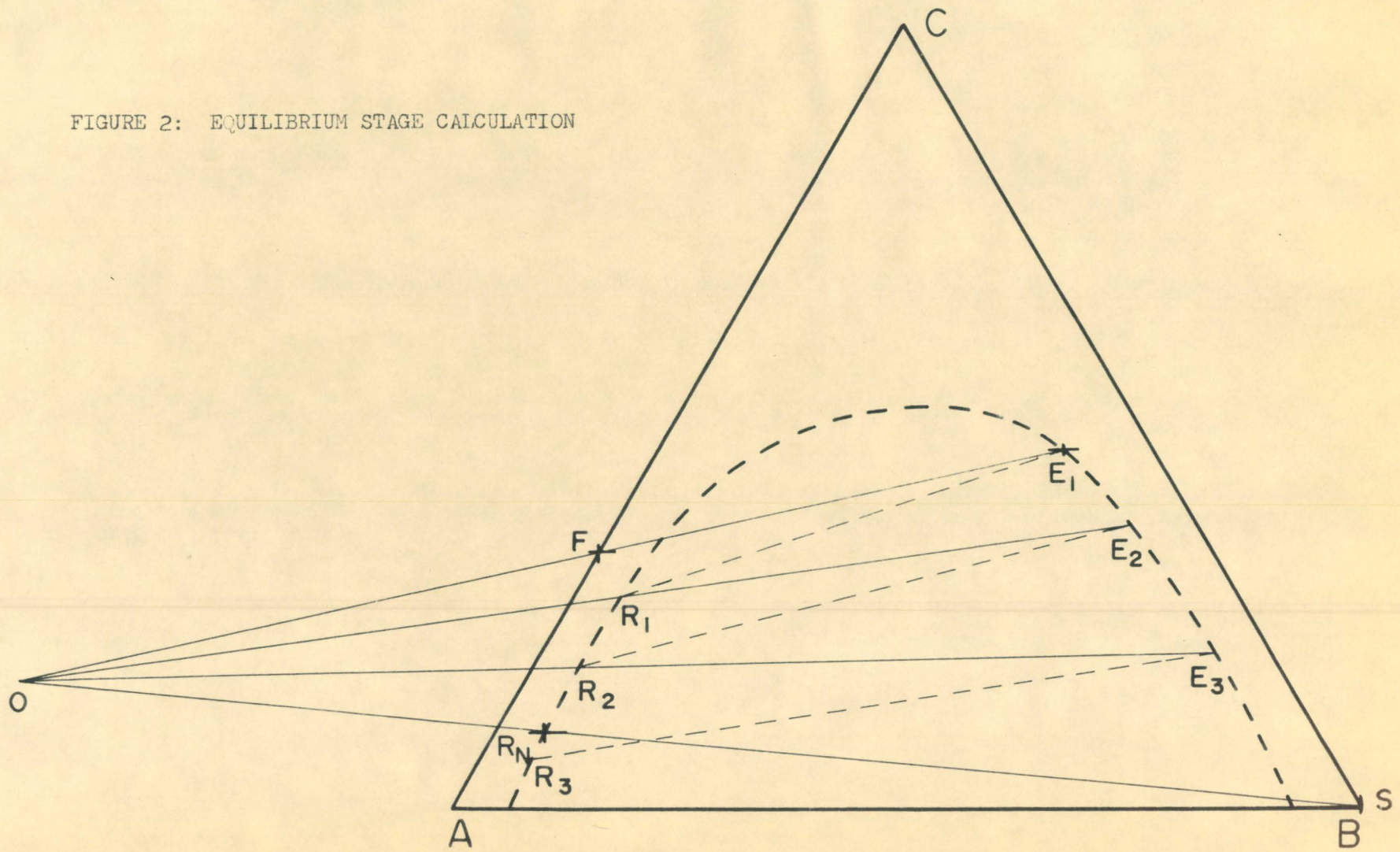
the equilibrium stage with that of the non-equilibrium stage has been made; both models can yield steady - state concentration profiles through the column as well as terminal concentrations.

Biery and Boylan (6) outlined a number of models by which they attempted to simulate the startup behaviour of a pulsed column. The simplest model, that of a non-equilibrium, ideally - mixed stage is described next.

In the formulation of this model, shown in Figure 3, the following assumptions are made:

(1) ideal mixing occurs in each phase of each stage

(2) solvent flow rates are constant

(3) holdups of dispersed and continuous phases are constant.

The first assumption means that the leaving concentration of a phase represents the average composition of the holdup, while the last two eliminate mutual solubility of the solvents. The following differential equations can now be written to describe the mass transfer between the two phases for a one stage representation of the column:

$$Tx_F - Tx_1 - K_E aV(y_1^* - y_1) = WR \frac{dx_1}{dt}$$

$$Uy_S - Uy_1 + K_E aV(y_1^* - y_1) = WE \frac{dy_1}{dt}$$

(8)

where T and U, the raffinate and extract phase flow rates respectively, are expressed as grams of solute - free phase per minute and WR and WE, the raffinate and extract holdups, are defined as grams of the corresponding solute - free phase. The raffinate and extract concentrations, x and y, are then expressed as grams of solute per gram of solute - free phase. For each additional stage used in the attempt to describe the

$$T x_F - T x_I - (K_E a) V (y_I^* - y_I) = W_R \frac{d x_I}{d t}$$

$$U y_S - U y_I + (K_E a) V (y_I^* - y_I) = W_E \frac{d y_I}{d t}$$
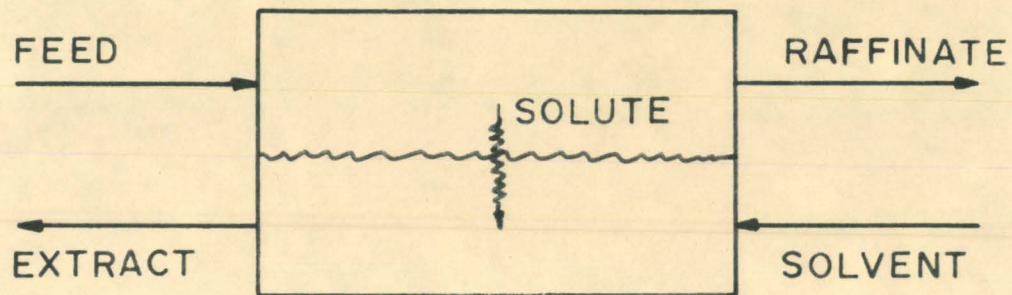
FIGURE 3: NON-EQUILIBRIUM STAGE

process, another pair of equations is added to the set (8). If steady - state concentrations only are desired, the concentration derivatives could be equated to zero and the resulting set of algebraic equations solved. In this study, the differential equations were solved since the transient response characteristics were also of interest.

II   SCOPE OF THE INVESTIGATION

(1)   In order to test methods of data representation as well as to obtain a criterion of extraction efficiency, a procedure for calculating the number of equilibrium stages on a digital computer was developed.   The methods involved were used in the initial study of simulation as techniques incorporated into the transient model.

(2)   Experimental methods of operation, using the system methyl isobutyl ketone, acetic acid and water, were developed to allow transient and steady - state measurements to be made on a Scheibel column. Values of the experimentally determined parameters were subsequently used in the theoretical model.

(3)   A mathematical model for the transient behaviour was then used to test the importance of variables as well as to indicate where more detailed work must be concentrated before a realistic model capable of prediction can be formulated.

III EXPERIMENTAL

3.1 System

The three component system – water, acetic acid, and methyl isobutyl ketone (MIBK) – was used in all calculations and experimental work. Solubility and equilibrium data were selected from the literature (7, 8, 9, 10, 11) with major emphasis on the work of Karr and Scheibel (11).

Table 1 lists the data used in the calculations while Figure 4 shows the ternary solubility diagram for this system. From the latter, the low selectivity and medium capacity are apparent.

TABLE 1:   SOLUBILITY AND EQUILIBRIUM CONCENTRATIONS

WEIGHT PER CENT

Equilibrium		Raffinate			Extract		
EC	RC	RA	RB	RC	EA	EB	EC
0.01	0.01	97.80	2.00	0.20	2.40	97.10	0.50
0.30	0.50	97.00	2.00	1.00	2.68	95.56	1.76
0.83	1.40	95.17	2.02	2.81	2.80	95.04	2.16
1.76	2.81	94.55	2.05	3.40	3.02	93.98	3.00
2.16	3.40	92.00	2.12	5.88	3.25	92.80	3.95
3.01	4.60	91.26	2.16	6.40	3.39	92.24	4.37
3.95	5.88	89.70	2.30	8.00	4.05	89.58	6.37
4.37	6.40	88.60	2.43	8.97	4.41	88.19	7.40
5.25	7.60	86.80	2.60	10.60	5.04	86.12	8.84
6.32	8.97	85.50	2.73	11.77	5.88	83.65	10.47
7.53	10.40	83.35	3.00	13.65	6.60	81.40	12.00
8.84	11.77	80.65	3.35	16.00	7.50	78.90	13.60
10.47	13.65	77.91	3.72	18.37	8.23	76.77	15.00
11.78	15.00	76.80	3.90	19.30	8.75	75.33	15.92
13.68	17.00	73.47	4.53	22.00	9.21	74.19	16.70
15.05	18.37	70.52	5.28	24.20	10.78	69.92	19.30
15.97	19.30	64.10	7.30	28.60	12.30	66.00	21.80
18.85	22.00	59.50	9.40	31.10	13.77	62.53	23.70
20.60	23.60	54.60	12.50	32.90	16.00	58.00	26.00
21.70	24.60	53.30	13.43	33.27	18.60	53.50	27.90
24.40	27.00	48.60	17.20	34.20	21.30	49.20	29.50
27.80	30.00				25.20	43.60	31.20
31.52	33.27				28.55	39.25	32.20
					34.56	32.20	33.20
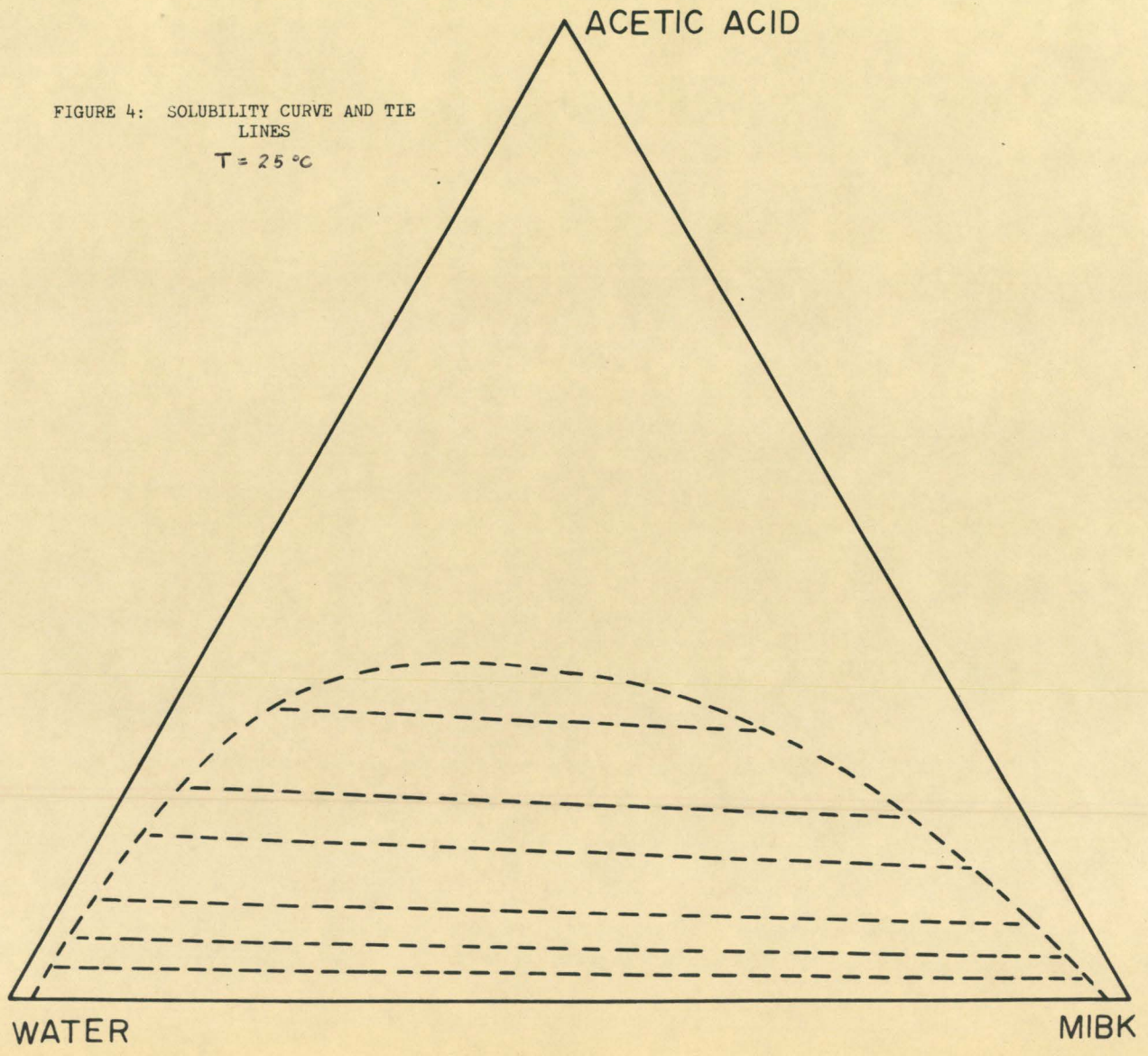
FIGURE 4: SOLUBILITY CURVE AND TIE LINES

T = 25 °C

ACETIC ACID

WATER

MIBK

13

3.2 Apparatus

A Scheibel mixer - settler column (12) with 24" between inlets, an inside diameter of 1 1/2", and 6 mixing sections was operated with countercurrent flows. Column level was controlled by means of a raffinate overflow device. Figure 5 is a schematic diagram of the apparatus.

For all experimental runs the water - acetic acid feed was used as the continuous phase while the dispersed phase consisted of the solvent, MIBK.

The following parameters were controlled by the experimental procedure:

(a) flow ratio, i.e., feed flow/solvent flow; FF/FS

(b) feed flow rate, FF

(c) agitator r.p.m.

(d) feed concentration, FC

(e) solvent concentration, SC

The criteria of operation which were used to characterize the runs were as follows:

(a) stage efficiency

(b) mass - transfer coefficient

(c) holdup volumes

The main experimental measurements and methods are listed below:

(a) concentrations of acetic acid in the feed, extract, raffinate and solvent were determined by titration with 0.1 N NaOH

(b) the densities of these four solutions were measured by displacement

STORAGE TANKS

SOLVENT   FEED

ROTAMETERS

E   R

SCHEIBEL
COLUMN

DRAIN
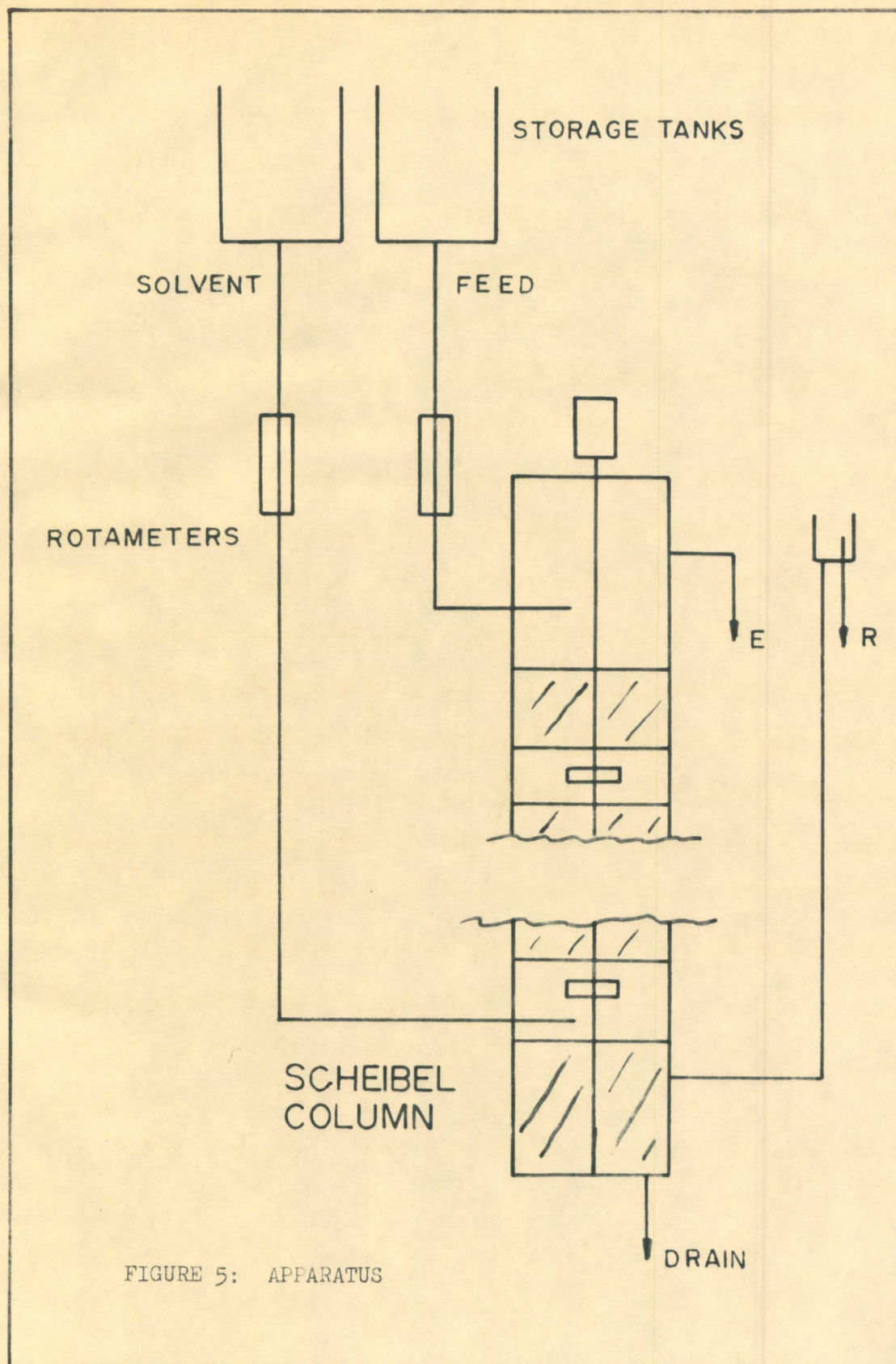
FIGURE 5:   APPARATUS

(c) separation by settling, after steady - state conditions were attained, allowed estimation of the dispersed and continuous phase holdups

(d) a stroboscope was used to measure the agitator speed

(e) feed and solvent flow rates were obtained from rotameter settings

(f) values of the extract and raffinate flow rates were assessed from timed collections in graduated cylinders.

Initial experiments determined that a minimum of five column displacements were required before steady - state conditions were reached. For transient operation a step change in the feed flow rate was introduced after one steady - state condition was reached and the column then run until a new steady - state was attained. Samples were collected at two minute intervals from the raffinate overflow bulb and from the extract overflow shown in Figure 5. The subsequent efficiency calculations, as with all calculations in this report, were programmed on the IBM 7040 computer.

A detailed experimental procedure is given in appendix II and complete program listings in appendix IV.

IV   CALCULATIONAL PROCEDURES

4.1   Data Representation By Table Look - Up

Figure 6 is a Bachman plot of the tie line data for the system water - acetic acid - MIBK. The system is not particularly well behaved and although regression analysis could be carried out to provide an analytical expression for the data, the equation produced could not be extended to other systems. Similar but greater difficulties exist for the representation of the binodal curve which is a two-valued function of component C.

To overcome these difficulties, both the tie line and solubility data were placed in arrays and an interpolation subroutine employed. Since such data are usually unequally spaced, the Lagrangian interpolation polynomial (13, 14, 15, 16) was used for the look - up procedure. By this method concentrations in either phase can be calculated from a single measured or computed value. The equation used in the interpolation is shown below:

$$Y = \sum_{i=1}^{n} \left(\prod_{\substack{j=1 \\ j \neq i}}^{n} \frac{x - x_j}{x_i - x_j} \right) y_i \tag{9}$$

Since round - off errors increased with additional terms, the interpolation was restricted to a sixth order polynomial. This loss of accuracy results from the repeated sums and products indicated by

FIGURE 6: BACHMAN PLOT FOR WATER — ACETIC — ACID — MIBK

EB/RA

EB

18
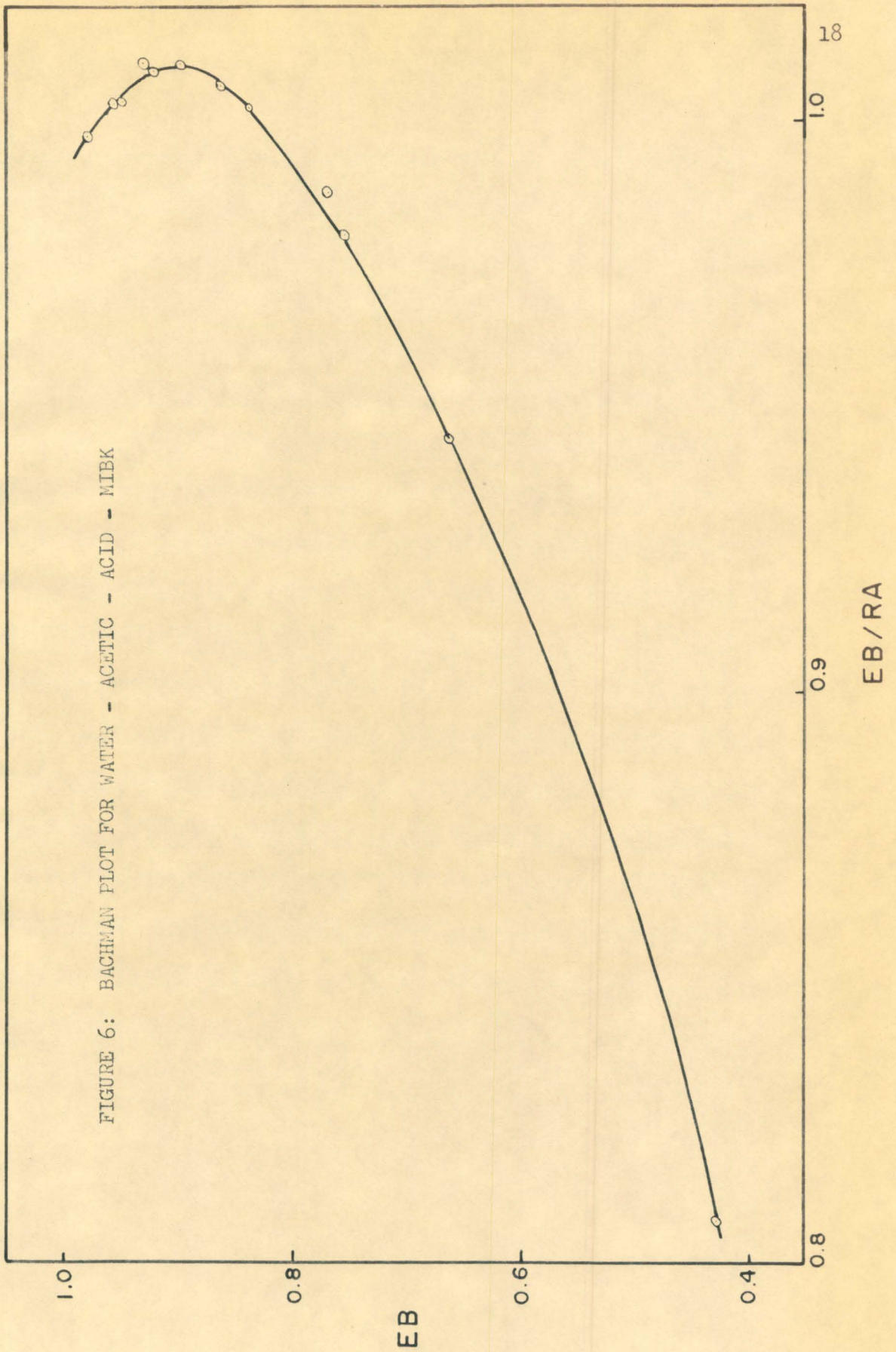
equation (9), and from the subtraction of numbers of equal magnitude in the numerator and denominator. By eliminating a table of differences, Lagrangian interpolation greatly reduces the computer storage problem. However, the main advantage of this method of data representation is its generality; other than perhaps some initial smoothing of the experimental data, the concentrations are arranged simply in tables.

Figure 7 illustrates the logic flow for the interpolation. Prior to this calculation a test must be made to determine the location of the argument within the range of the array. This information is necessitated by the restriction to sixth degree interpolation; three concentrations are used on each side of the argument, except at the ends of the table.

Several important aspects of the calculation of the number of theoretical stages can now be solved by using one general interpolation subroutine. Starting with any concentration of component C in one phase, the equilibrium concentration in the other phase can be found. This amounts to moving from one end of the tie line to the other. Secondly, by knowing the concentration of any one component of a phase the other two can be computed. This last procedure plays an important part in the next calculation.
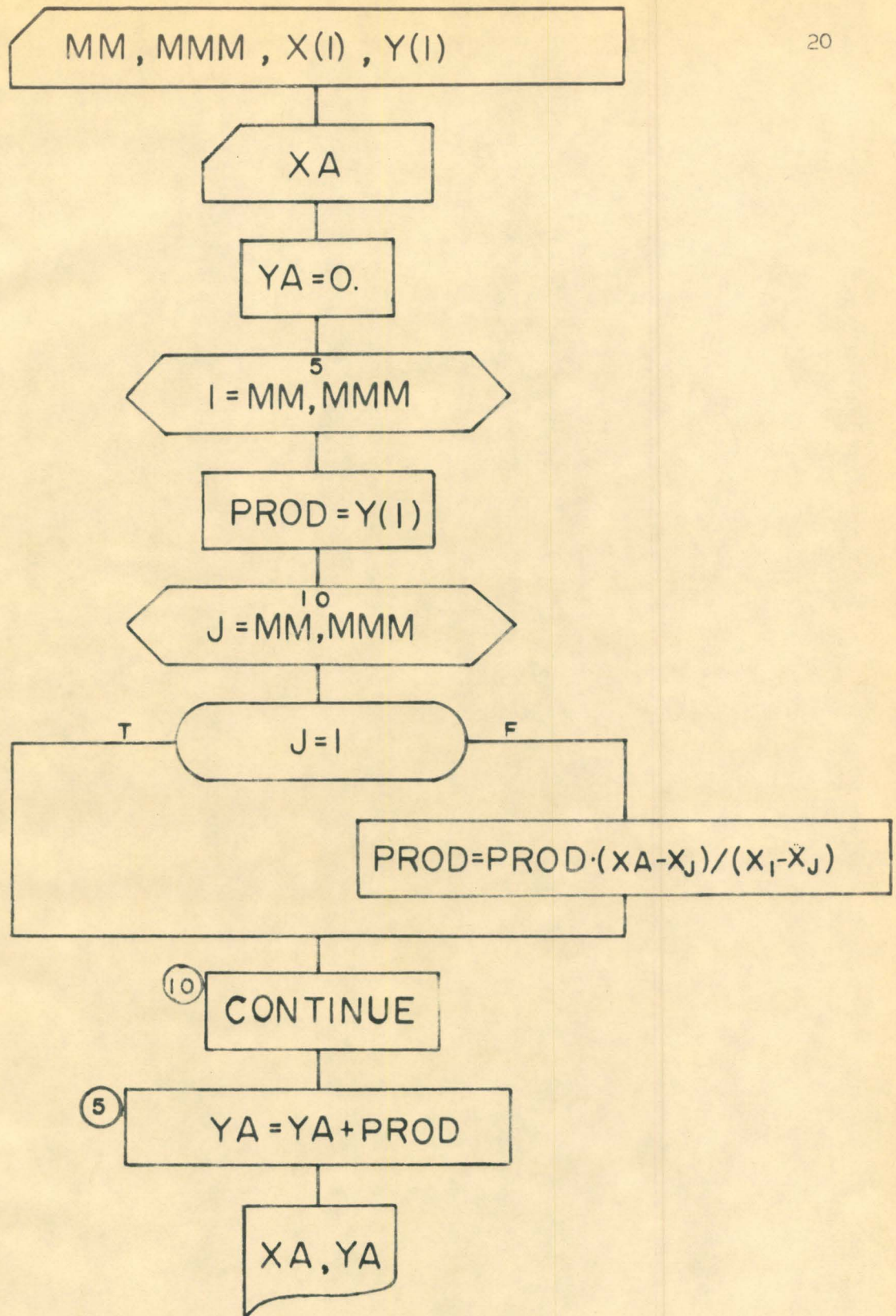
FIGURE 7: LAGRANGIAN INTERPOLATION

4.2 Fibonacci Search Scheme for Flows

The search scheme for flows and concentrations can be described by referring to stage 1 of Figure 1. The following parameters are known experimentally: the flow rates and concentrations of the feed F, solvent S, extract E_1 and raffinate R_N. For the first stage the flows and concentrations of R_1 and E_2 are unknown. However, the weight percent of the components of R_1 can be found from E_1 by interpolation.

The evaluation of the concentration in the other stream, E_2, involves a trial and error procedure. A flow FR_1 is assumed and this allows the flow of E_2, FE_2, to be calculated. The concentrations of E_2 can then be obtained from a material balance. For example:

$$EA_2 = (FR_1 \cdot RA_1 + FE_1 \cdot EA_1 - FF \cdot FA)/FE_2 \tag{10}$$

Using this concentration of water, the Lagrangian interpolation procedure can be utilized to predict the corresponding concentration of acetic acid, EC_2. However, EC_2 can also be predicted directly from a material balance similar to equation (10). The difference between these two values forms the criterion for the accuracy of the flow assumption. By taking the absolute value of the difference, a unimodal function with a minimum of zero can be produced. The form of the curve is shown in Figure 8.

Assuming that a range containing the correct flow FR_1^* can be found, a Fibonacci search (17) can then be carried out on this curve to locate FR_1^* by using the minimum value of $|\Delta EC_2|$ as the indicator.

The following is a brief summary of the features and fundamental concepts of the Fibonacci search.

Assume that the flow range is defined by $(FR_1)_0$ and $(FR_1)_N$ and
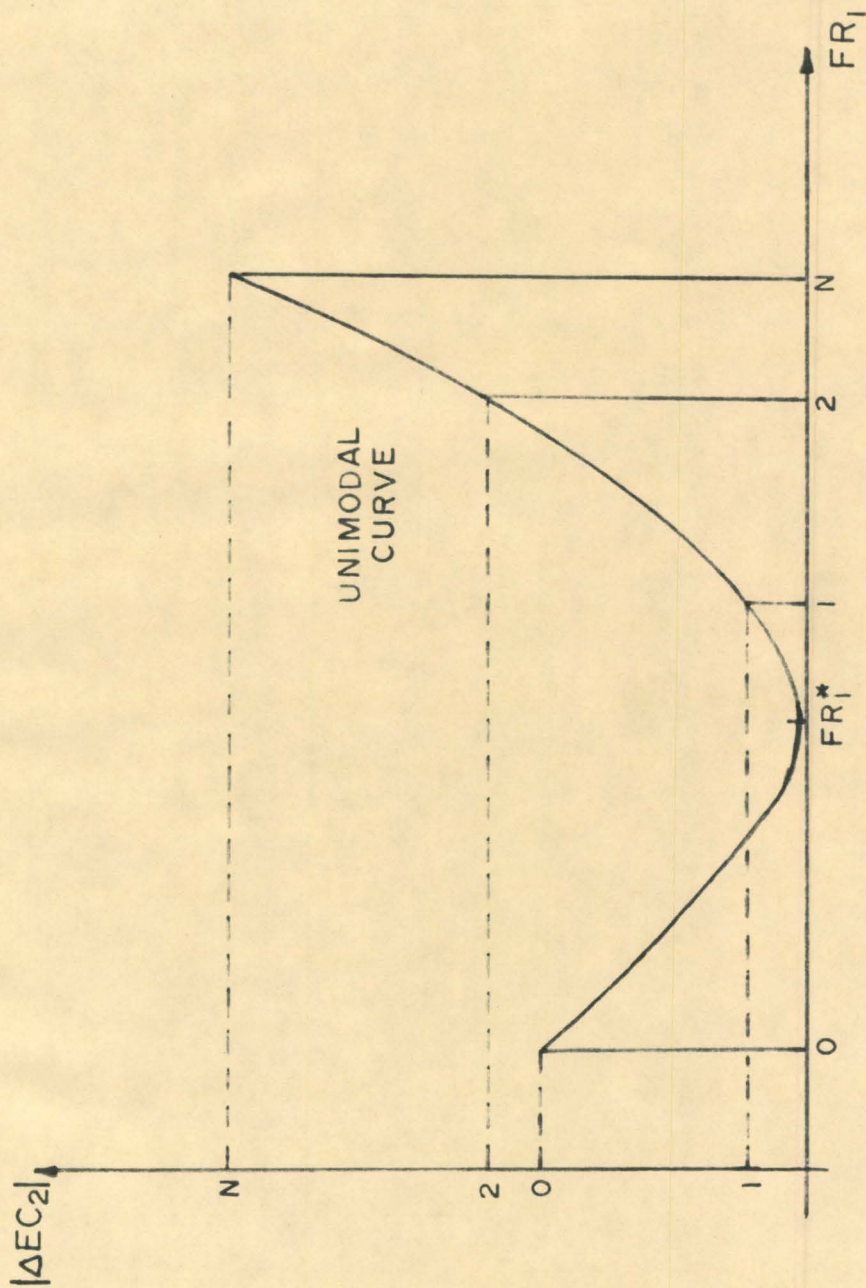
FIGURE 8: SEQUENTIAL SEARCH

that the corresponding $|\Delta EC_2|_0$ and $|\Delta EC_2|_N$ have been evaluated. Consider two trial flows $(FR_1)_2 > (FR_1)_1$. By referring to Figure 8 and recalling that the function is unimodal, three possibilities become apparent:

(1) $|\Delta EC_2|_1 < |\Delta EC_2|_2$

(2) $|\Delta EC_2|_1 > |\Delta EC_2|_2$

(3) $|\Delta EC_2|_1 = |\Delta EC_2|_2$

If the case (1) held, the optimum, in this example a minimum, could not lie to the right of $(FR_1)_2$ without contradicting the assumption that the curve is unimodal. Hence

$$(FR_1)_0 \leq FR_1^* < (FR_1)_2 \tag{11}$$

Similarly if case (2) holds then

$$(FR_1)_1 < FR_1^* \leq (FR_1)_N$$

These two cases, when analyzed together, cover the third possibility; i.e., when equal, the optimum must lie between $(FR_1)_1$ and $(FR_1)_2$.

This example illustrates the basic concept of a sequential search. Starting with an initial calculation, a second estimate within the same restricted range allows the optimum to be enclosed by a smaller interval. Now, a single, new calculation within this latest enclosure will again reduce the interval of uncertainty. This procedure when carried out in an optimal manner constitutes the Fibonacci search.

One of the prime features of this plan is that by specifying the location of the first calculation, L_1, the entire Fibonacci search is defined. This technique is most efficiently continued by placing

the next calculation symmetrically with respect to the one already in the interval. The placement of the first assumed flow depends upon the total number of calculations, N, being known in advance. However, specification of N allows the final range of uncertainty, L_f, to be stipulated.

The determination of L_1, L_f, and N is outlined next. First, the Fibonacci series must be defined; the general equation is given as (13).

$$F_n = F_{n-1} + F_{n-2} \, , \, n > 2 \tag{13}$$

By definition $F_0 = F_1 = 1$.

Then from (13) $F_2 = 2$, $F_3 = 3$, $F_4 = 5$, $F_5 = 8$, etc.

The derivation of the following three equations is outlined by Wilde (17). The calculation of the initial placement is based on equation (14):

$$L_1 = \frac{F_{N-1}}{F_N} + \frac{(-1)^N \epsilon}{F_N} \tag{14}$$

L_1 is thus the fraction of the original interval at which the first assumed flow, $(FR_1)_1$, is situated. ϵ is defined as the least separation between two calculations for which a difference between $|\Delta EC_2|_1$ and $|\Delta EC_2|_2$ can be detected. The fraction of the original range remaining after N calculations can be predicted from equation (15):

$$L_f = \frac{1}{F_N} + \frac{F_{N-2}}{F_N} \cdot \epsilon \tag{15}$$

While the actual value of N is subject to choice the limiting value is specified by equation (16). This maximum number is naturally dependent upon the distinguishability of the calculations.

$$N_{max} \leq 4.785 \log \left(\frac{L_0}{\epsilon}\right) - 0.328 \qquad (16)$$

where L_0 is the original interval. The logic flow diagram of the Fibonacci search is shown in Figure 9.

Two aspects of this technique should be emphasized: first, the range which is optimized is FR_1 not $|\Delta EC_2|$; second, by choosing the total number of calculations in advance, the program automatically stops at the predetermined accuracy. A numerical example which shows the power of this search is given in appendix III.
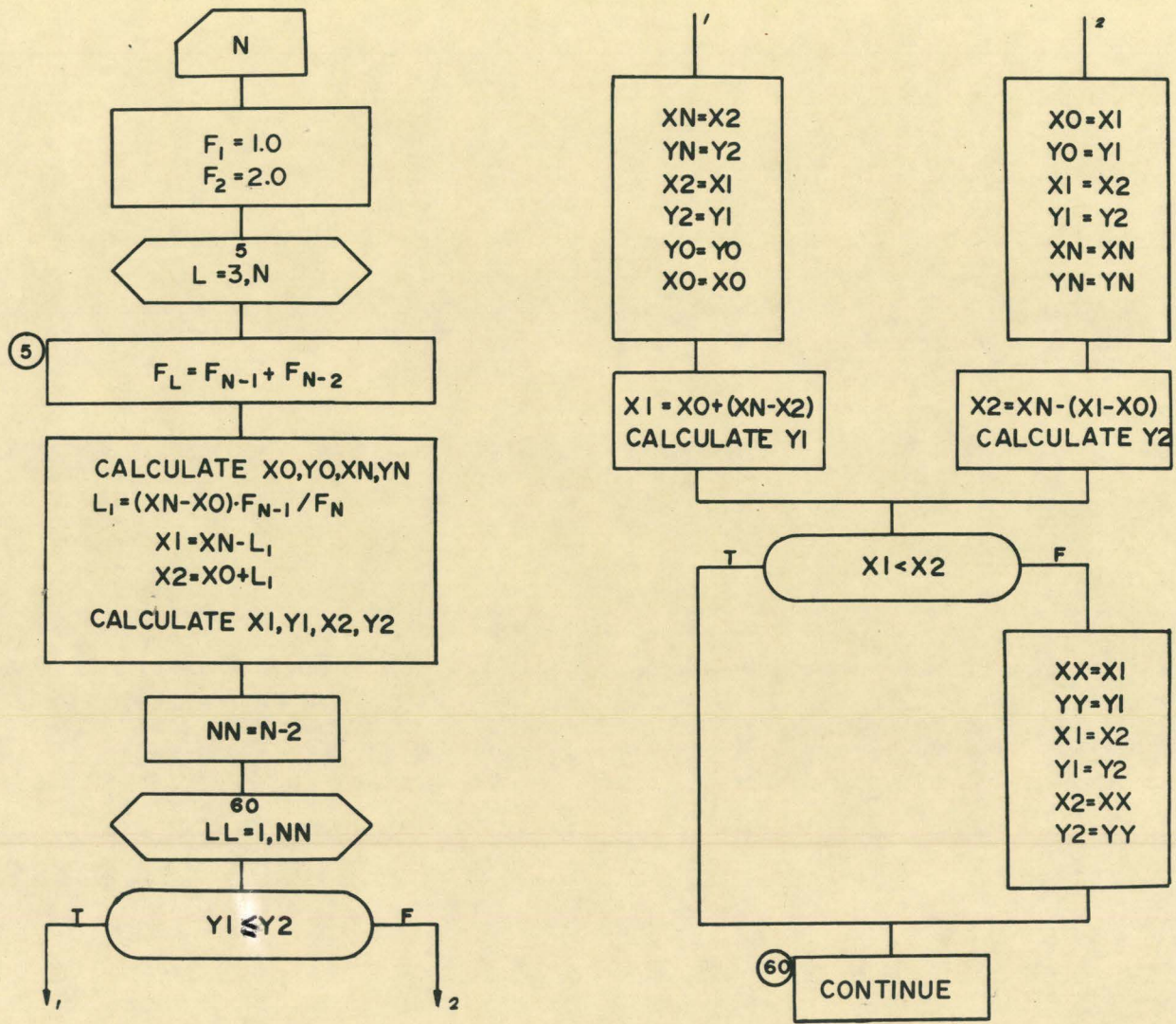
FIGURE 9: FIBONACCI SEARCH SCHEME

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4.3 Summary of Theoretical Stage Calculation

The concentration of acetic acid, the volume flow rate and the density of the feed, solvent, extract and raffinate are determined experimentally. EA_1 and EB_1 are then found by interpolation from EC_1. From the table of tie line concentrations, RC_1 is obtained and then from this value, RA_1 and RB_1 are determined. At this point, the range of FR_1 is defined by restricting it to values which make all flows positive and then by choosing the flows which produce the maximum and minimum concentrations of RA_1 in the solubility table. The Fibonacci search is then carried out within this range to determine the correct value of FR_1. Since this technique determines a final interval of uncertainty, the mid-point of L_f is chosen as the optimum value. Next, an overall balance determines FE_2 while a component balance determines EA_2. From this last concentration EC_2 and EB_2 are found by interpolation. Now the calculation is repeated using EC_2 to find the equilibrium concentration RC_2. Each time RC_J is calculated it is tested against RC_N. If the calculated value is less, then linear interpolation proceeds to determine the fractional number of stages. From this, the efficiency of the extraction process is determined as the number of theoretical stages divided by the number of actual stages.

So far, all discussion has been based on a calculation starting from E_1 and proceeding to R_N. However, a similar computation can be made by using R_N as the initial concentration, and thus the efficiency from the former method can be checked against that of the latter.

4.4 Transient Model of Non-Equilibrium Stages

From equations (8), the following set of equations can be
written to apply to any general stage i:

$$Tx_{i-1} - Tx_i - K_E a\, V_i (y_i^* - y_i) = WR_i \frac{dx_i}{dt} \tag{17}$$

$$Uy_{i+1} - Uy_i + K_E a\, V_i (y_i^* - y_i) = WE_i \frac{dy_i}{dt}$$

The Runge - Kutta - Gill (18) procedure was used to integrate these
equations. Elimination of the restriction of a linear equilibrium re-
lationship was facilitated by the Lagrangian interpolation subroutine;
for each value of x_i, either intermediate or final, in the Gill method,
a corresponding y_i^* was found.

In using this method, certain problems arise concerning the
estimation of the experimental parameters necessary for the solution of
the differential equations. While the total column volume and total
phase holdups are easily measured, the distribution of the individual
stage holdups is unknown. Another problem is the dependence of the
mass - transfer coefficient, $K_E a$, on concentration. However, for many
systems this dependence is small and since the actual concentration
profile in the column is unknown, the coefficient is calculated on the
following overall basis (5). First, NTU_{OE} was calculated from equation
(18) which is based upon a differential change throughout the column:

$$NTU_{OE} = \int_{EC_1}^{EC_2} \frac{dEC}{EC^* - EC} + \frac{1}{2} \ell n \left(\frac{100 - EC_1}{100 - EC_2} \right) + \frac{1}{2} \left(\frac{EC_1(r-1)+100}{EC_2(r-1)+100} \right) \tag{18}$$

where r is the ratio of the molecular weights of the nonsolute to solute. This equation, which assumes immiscible solvents, is evaluated by graphically integrating the first term. The mass - transfer coefficient can then be calculated from equation (19):

$$K_E a = NTU_{OE} \cdot U/V \qquad (19)$$

Now, two possibilities arise for the stagewise simulation based on equations (17). First, the experimentally determined variables can be substituted directly into the model. Then, the problem is to find the correct number of stages which will accurately reproduce the column behaviour; in particular the steady - state terminal concentrations and the transient response curves. With this method the physical operation of the column is neglected and the column is treated as a "black box". This means that the number of stages is arbitrary for a particular set of operating conditions but will vary as conditions such as agitator r.p.m., flow rates and inlet concentrations vary. However, given a set of operating variables there is no 'a priori' method at present of predicting the number of stages required for the column simulation.

The second method considers the physical construction and operation of the column and thus the premise is made that there are six well - mixed stages in the model since there are six mixing - settling sections in the actual column. Here the problem is to find a particular $K_E a$ which will then make the model reproduce the experimental concentrations.

Using either method and starting with any particular number of stages and any given set of parameters, a concentration profile can be calculated and the terminal concentrations and transient response curves

compared with the experimental values. These comparisons then form the criterion of model adequacy.

V DISCUSSION OF RESULTS

Detailed experimental and calculational results are presented in appendix III.

5.1 Calculation of Equilibrium Stages

While it would be expected that the stage efficiency is independent of calculation direction, either E_1 to R_N or R_N to E_1, Table 2 illustrates the differences found for various experimental conditions.

TABLE 2: COMPARISON OF STAGE EFFICIENCIES FOR TWO DIRECTIONS
OF CALCULATION AND VARIED OPERATING CONDITIONS

Agitator r.p.m. ranged from 240 to 580
Feed concentration varied from 5 wt % to 20 wt %
Feed/Solvent flow ratio varied from 4 to 0.7

Efficiency		Difference	Acetic Acid
Direction of Calculation		Between	Balance
E_1 to R_N	R_N to E_1	Efficiencies	(%)
44.34	46.07	1.7	1.62
37.92	35.84	2.1	0.91
37.04	35.68	1.4	0.82
35.40	37.64	2.2	0.10
53.18	49.23	4.0	-3.15
55.03	60.85	4.8	3.02
46.76	38.80	8.0	-4.37
59.51	38.71	20.8	-6.82
67.67	58.30	9.4	0.71

From this tabulation a number of conclusions can be drawn:

(i) Those experiments with the smallest solute imbalance have the closest agreement between efficiencies. The last entry in the table is explained in section (iii) below.

(ii) These calculations lead to the result that the maximum tolerable acid imbalance is approximately 2.5% for this system. Beyond this value, the criterion of stage efficiency must be suspect.

(iii) The last entry represents the effect of operation at a limiting physical condition. The feed flow rate of 61.8 gms/min is much larger than the 14.1 gms/min of solvent for this particular run. Consequently, the concentration change from feed to raffinate is very small - 20.30 to 16.55. With the relatively flat tie lines of the system water - acetic acid - MIBK, a change of only 4% makes it imperative that all concentrations be known as accurately as possible. As proof of this importance, consider Table 3 which shows the effect of a variation in the second decimal of the experimentally determined extract and raffinate concentrations for this particular experiment.

TABLE 3: EFFECT OF SECOND DECIMAL VARIATION FOR HIGH FLOW RATIO

EC	RC	Efficiency		Difference
		E_1 to R_N	R_N to E_1	
16.75	16.55	67.67	58.30	9.4
16.77	16.55	72.85	59.92	12.9
16.79	16.55	91.12	61.55	30.6
16.75	16.53	67.70	60.60	7.1
16.75	16.50	67.75	63.98	4.8

Flow Ratio = 61.8/14.1; Feed Concentration = 20.3 wt%

Besides showing the magnified effect of small variations, this table also shows the importance of the initial concentration for either direction of calculation. These results can be contrasted with those given in Table 4 where the effect of the same magnitude of variation is shown for the first entry in Table 2. This run had a smaller flow ratio than the above (62.0 gms/min of feed to 39.8 gms/min of solvent).

TABLE 4:   EFFECT OF SECOND DECIMAL VARIATION FOR MEDIUM FLOW RATIO

EC	RC	Efficiency		Difference
		E_1 to R_N	R_N to E_1	
12.60	9.55	44.34	46.07	1.7
12.62	9.55	44.75	46.21	1.5
12.64	9.55	45.17	46.34	1.2
12.60	9.53	44.40	46.28	1.9
12.60	9.51	44.47	46.51	2.0

Flow Ratio = 62.0/39.8;   Feed Concentration = 17.9 wt%

(iv) The variation between the efficiencies for the two directions of calculation is a direct function of the system. For components with greater selectivity and higher capacity, the high experimental flow ratio would not produce as large a fluctuation for the same small concentration variations.

(v) While Table 2 presents only the acetic acid balance it should be noted that the overall material balance will also affect the results. However, since acetic acid is used as the key component in the calculation, then discrepancies in the acid concentration will obviously have the largest effect on the calculations. Also since four streams are involved in the material balance, then closure will not automatically

ensure reproducible results. For example, the two inlet streams may both be in error with one high and one low measurement but the total may be correct due to compensating errors.

5.2 Prediction of Steady - State Concentrations From Transient Model

5.2.1 Arbitrary Number of Stages

Two different effects were found when the model incorporated the mass - transfer coefficient which had been calculated from experimental concentrations. First, those experiments with high flow ratios and a high degree of mixing required only a limited number of stages in order to reproduce the experimental concentrations. Conversely, those with low or medium ratios required a very large number of stages for an adequate representation of the column. Figure 10 illustrates the differences in the approach to the experimental raffinate concentrations as the number of stages in the model is increased.

With the high ratio, the model closely approximated an equilibrium stage simulation. This can be seen, in Table 5, by the effect that changes in $K_E a$ produced in the terminal concentrations for four, five and six stage models. Since no further concentration change occurs for variations in $K_E a$, then the driving force, $(y_i^* - y_i)$, must be very small i.e., equilibrium has been reached. Also the four to six stage representation compares relatively closely with the number of calculated equilibrium stages - approximately four for these particular operating conditions. Physically, this behaviour results from a high agitator r.p.m. of 580 as well as the small solvent flow compared to the feed

FIGURE 10: PREDICTION OF STEADY - STATE CONCENTRATIONS

Raffinate Concentration vs. Number of Stages

0.1345 High Flow Ratio

0.1230 Medium Flow Ratio

0.0963 Low Flow Ratio

X
gms solute/
gm solute-free
raffinate

Number of Stages
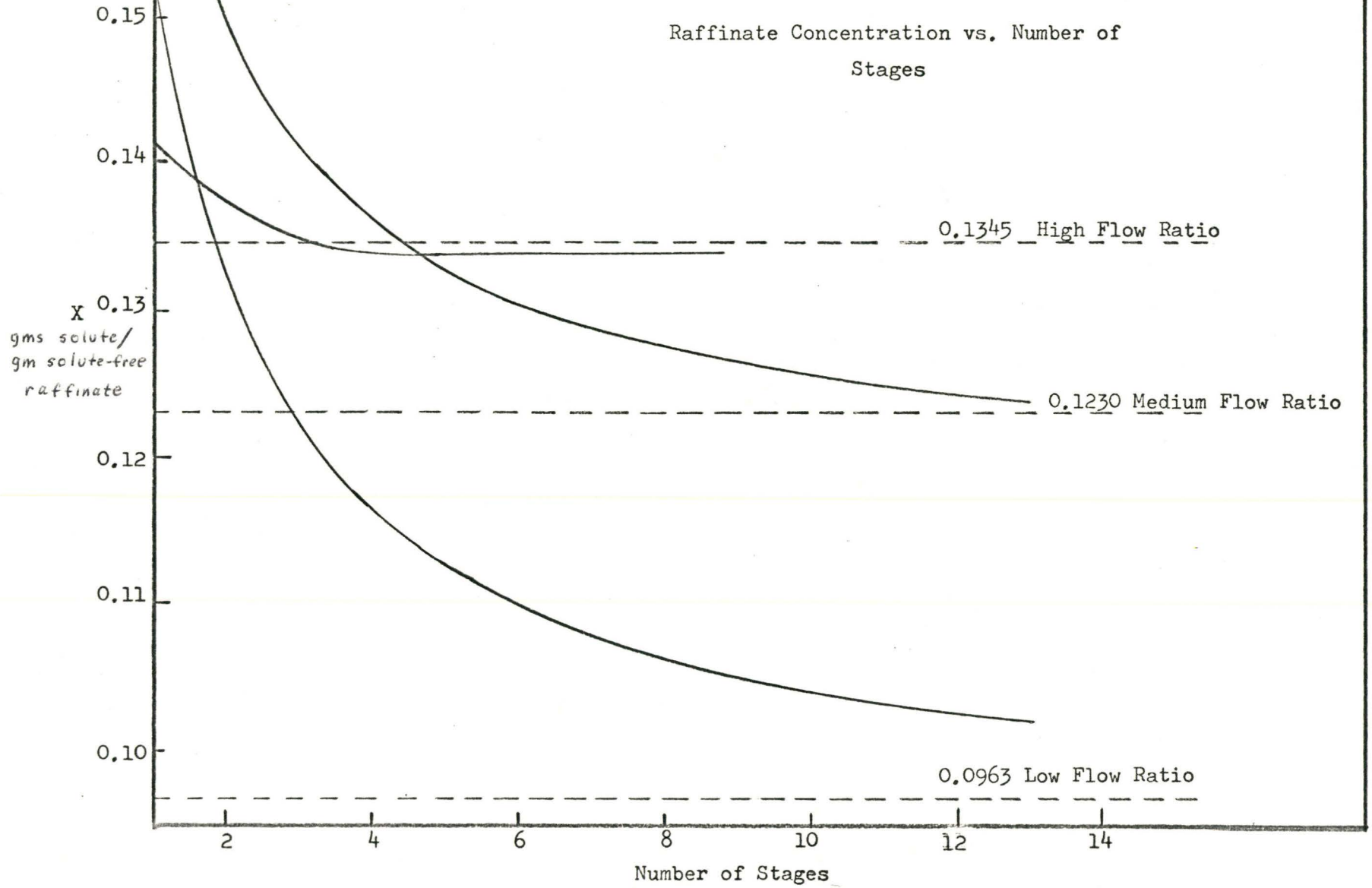
flow. Consequently the K_Ea was found to be considerably higher at 0.174 than those calculated from experiments with lower flow ratios and agitator r.p.m.

TABLE 5:   EFFECT OF K_Ea FOR HIGH FLOW RATIO

No. of Stages	K_Ea	Concentrations	
		X, Raffinate	Y, Extract
4	0.174	0.1344	0.1196
5	0.174	0.1340	0.1210
6	0.174	0.1338	0.1219
4	0.164	0.1345	0.1192
4	0.194	0.1342	0.1202
6	0.164	0.1339	0.1215
6	0.194	0.1337	0.1223
Experimental		0.1345	0.1220

Feed flow rate = 52.5 gm/min
Solvent flow rate = 14.0 gm/min
Feed concentration = 0.1663
Solvent concentration = 0.00

As shown in Figure 10, those experiments with lower flow ratios and less mixing require essentially an infinite number of stages in order to reproduce the terminal concentrations. This results from the fact that the flows are sufficient to ensure a reasonable driving force throughout the whole column. Now, bearing this in mind, the transient model can be compared with the model used to define the overall transfer coefficient. Equation (20) represents the usual definition for an elemental volume dV.

$$dN = K_Ea \ dV \ (y^* - y) \tag{20}$$

Here y* is the concentration of an extract phase which would be in equilibrium with the bulk concentration of the raffinate phase. Now, both bulk concentrations, x and y, also represent the outlet concentrations for the element dV. That is, the defining model incorporates ideal mixing in both phases. K_Ea is then assumed independent of concentration so that it is held constant when equation (20) is integrated over the concentration range. Therefore, by using the measured overall K_Ea, which is then the same as the K_Ea for an element, and an ideally - mixed transient model, the representation becomes the same as the defining model, with the exception of the assumptions involved in calculating K_Ea from experimental terminal concentrations. In effect, the transient model must then have stages with a volume dV in order to get the correct total mass transfer or in other words an infinite number of stages is required.

5.2.2 Six Stage Representation

With runs operated at low and medium flow ratios, an attempt was made to find a K_Ea which would reproduce the steady - state concentrations when the model was restricted to six stages. Since a large number of stages was required when the model utilized the experimental K_Ea, then as the number of stages is decreased, the mass - transfer coefficient must be correspondingly increased in order to obtain the same total mass transfer. In particular, for low and medium flow ratios the following comparison can be made between the K_Ea calculated from experimental results and that used to make the six stage model fit the experimental results:

TABLE 6: $K_E a$ COMPARISON FOR LOW AND MEDIUM FLOW RATIOS

Flow Ratio	Experimental $K_E a$	Calculated $K_E a$
Low (35.9 / 38.0)	0.101	0.156
Medium (53.7 / 38.0)	0.143	0.212

The criterion for choosing the best $K_E a$ is provided by a least - squares approach to the differences between experimental and calculated concentrations.

5.2.3 Discussion

From the set of equations (17), it is apparent that values of WR and WE, the phase holdups, will not affect the steady - state terminal concentrations. Rather, these holdups only change the response characteristics of the model.

The results of sections 1 and 2 illustrate a very significant general principle: namely, that an estimate for the number of stages for one set of conditions has little bearing on another fairly different set of conditions when the arbitrary stage approach is used. Thus, section 1 shows the insignificance of trying to fit an arbitrary number of stages to a model representing actual column behaviour.

By comparing steady - state concentrations only, a means of reducing the number of variables in the transient model is obtained. That is, since terminal concentrations will be independent of phase

holdups then the only variables which need be considered at this point
are $K_E a$, V and the number of stages.

5.3 Transient Evaluation

In order to solve equations (17) an initial concentration pro-
file must be known. If an assumed profile is not correct then the
early part of the response curve will contain considerable fluctuations.
Since the comparison of the experimental and theoretical responses is
based on the ability of the model to predict the initial dead time as
well as the general curve shape and steady - state concentrations, the
starting values thus assume a large measure of importance.

To eliminate the difficulty of finding the correct profile, ex-
periments were run in pairs. The initial steady - state concentrations
of the transient run were measured before the flows were stopped to
allow phase holdup measurements to be obtained. The same operating
conditions were then maintained and the column run until the same steady -
state conditions again prevailed. At this point a step change in the
feed flow rate was introduced and the transient response followed by
sampling the extract and raffinate at two minute intervals. By this
method, even though the initial run was repeated, detailed evaluation
of the initial and final parameters could be obtained. The main dif-
ference between the initial and final steady - steady parameters in-
volved $K_E a$ (0.156 to 0.212) while the total volume changed only slightly
(705 to 710) as did WE (26.5 to 25.7) and WR (593 to 586).

Now, using the six stage representation, equation set (17) can
be solved using all measured variables, except the calculated six stage

$K_E a$, to produce an initial steady - state profile. This profile is then used as the initial estimate at the point when the upset is introduced. However, several important problems still remain; the most pressing concerns the change of $K_E a$ from 0.156 to 0.212 over the duration of the transient response. If an initial step in $K_E a$ were used, the concentration gradients would be extremely steep and no lag or dead time would be produced. To overcome this, the change in $K_E a$ was applied linearly over increments of time corresponding to some multiple of the time required for one volume displacement. Since the volumes V, WE and WR were very similar between the initial and final conditions, the model used the values of these three variables as measured at the end of the run. This simplification had little overall effect but it did reduce or eliminate additional fluctuations in the initial profiles.

The experimental and theoretical response curves are compared in Figures 11 and 12. Table 7 compares the times required to reach 63.2% and 98% of the steady - state values for Run 14.

TABLE 7: RESPONSE TIMES OF RUN 14

Volume Displacements Used for Change in $K_E a$	Time - minutes			
	$T_{63.2}$		T_{98}	
	Extract	Raffinate	Extract	Raffinate
Experimental	7.65	16.2	24.8	29.6
5	11.6	6.7	36.6	15.3
4	10.6	6.8	30.0	16.6
3	9.5	7.0	28.3	29.6
2	7.9	7.45	24.4	31.2

Feed flow = 53.7 gm/min
Solvent flow = 38.0 gm/min
Feed concentration = 0.246
Solvent concentration = 0.00
Agitator r.p.m. = 460
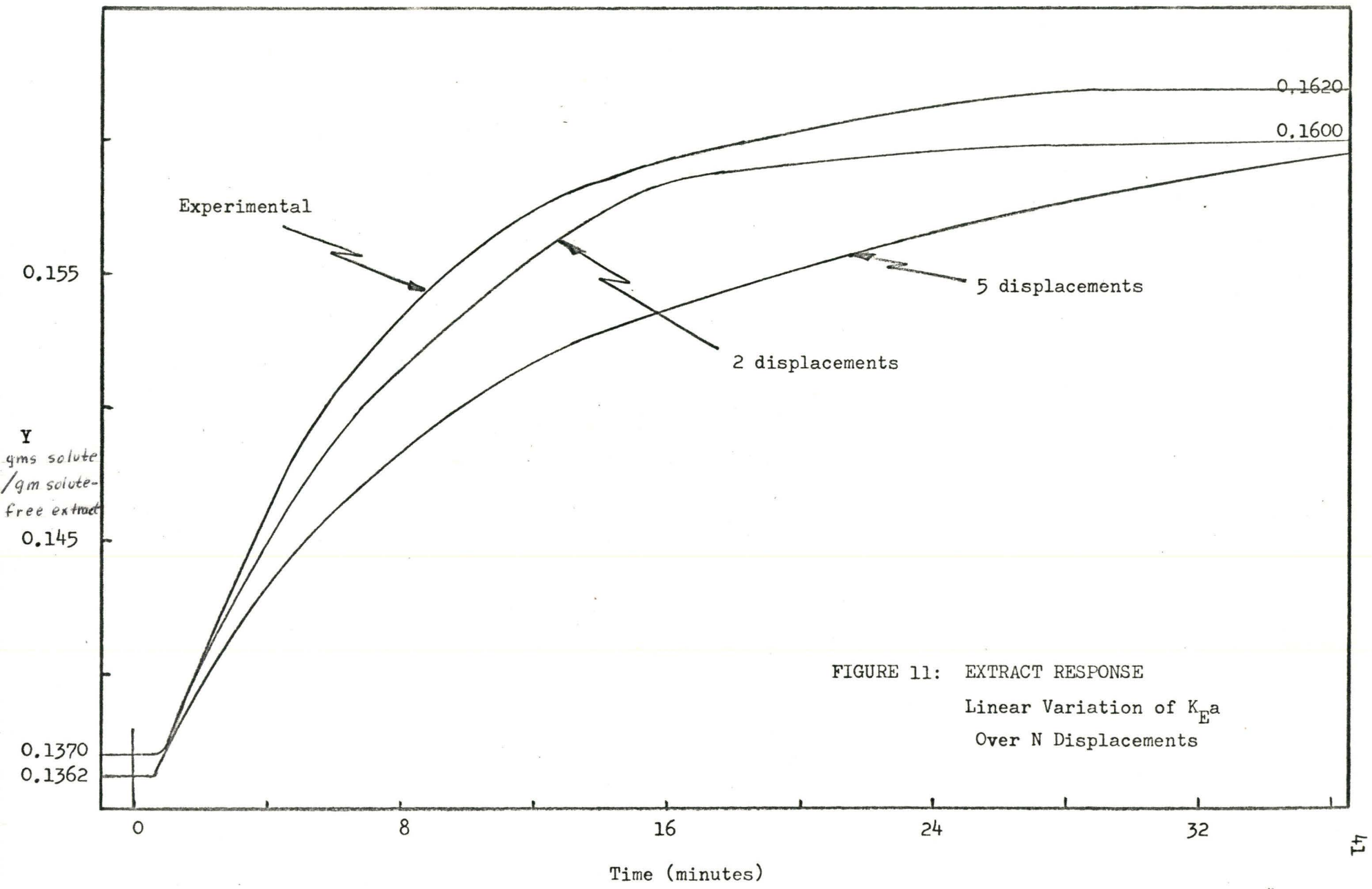
FIGURE 11:   EXTRACT RESPONSE

Linear Variation of $K_E a$

Over N Displacements
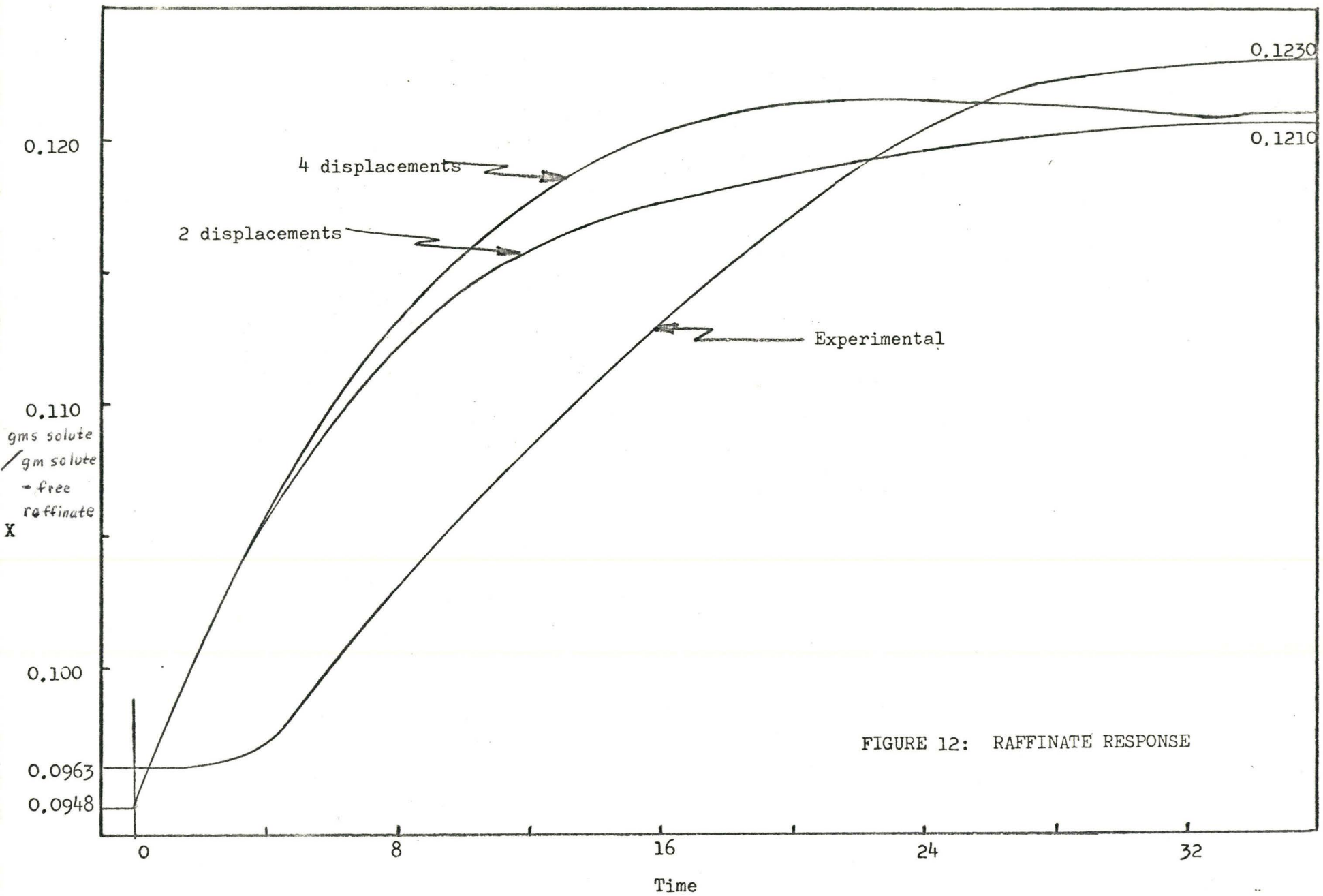
FIGURE 12: RAFFINATE RESPONSE

From the extract graph and the table it is apparent that the assumption of a linear change of $K_E a$ over a period of two displacements provides a reasonably good simulation. On the other hand, the raffinate curves and response times do not compare favorably. This inconsistent behaviour is due to the particular method of column construction and operation. By recalling that the raffinate samples are obtained from the raffinate overflow bulb, it becomes clear that a large delay can be produced. As well, this extra holdup serves as a mixing tank so that the net effect is to reduce the rate of change of concentration with respect to time and to shift the response by the delaying action. For the experiment shown in Table 7, there were 140 mls. of raffinate at the bottom of the column plus another 80 mls. in the raffinate level bulb and connecting tubing. Thus, with this 220 mls. of extra holdup and a feed flow rate of 53.7 mls./min. it would take approximately four minutes before a concentration change at the base of the column would be measured in the raffinate sample. As well, any disturbance in the feed conditions must travel down the column before it is detected in the raffinate. This rough approximation agrees well with the delay shown in Figure 11. Conversely, the extract has a relatively small holdup of about 45 mls. at the top of the column. Hence, with the solvent rate of 38.0 gm./min. and no large mixed holdup, little delaying effect is noticeable.

This discussion suggests that sampling should be made as close as possible to the regions of final phase separation. An alternative to this would be to consider the column as six stages in which mass transfer occurs plus an additional mixing tank for the raffinate phase.

It must be stressed that the dependence in the model of $K_E a$ on concentration, and consequently time, is arbitrary. Since no independent quantitative estimation of the effect of the agitator has been made, then for a different degree of mixing, the mass - transfer coefficient must be changed in a different manner. While the agitator speed is essentially incorporated into the coefficient, a better model should contain a separate term for mixing. This is difficult to do since the effect of the agitation on such parameters as drop size is a function of the feed concentration as well as the flow rates. That is, for higher concentrations of acetic acid, the interfacial tension decreases and the mixing can thus produce greater interfacial area.

Again, for a better model, some refinements in the change of phase holdups with flows and concentrations would be included.

Thus, this simple transient model, even though it embodies some arbitrary assumptions, has been sufficient to indicate the importance of the variables involved in the Scheibel column and to suggest improved or alternative methods of experimental operation.

5.4 Computation

(i) A single efficiency calculation using the equilibrium stage approach required a time of approximately 15 seconds. Compilation of this program occurred in less than 3 minutes.

(ii) For the calculation of steady - state and transient concentrations from the non-equilibrium model, about 2 minutes were required for compilation and approximately 6 minutes for a six stage representation to be run to steady - state. However, as the number of stages was increased

the computation time increased drastically at a rate of approximately one minute per extra stage. Computation time could be decreased by changing the integration procedure. A predictor - corrector method would probably give some saving and it has been reported by Rosenbrock (19) that some implicit methods can markedly cut integration time at the cost of some loss of accuracy.

(iii) It should be emphasized that the above times are for an IBM 7040 with an on-line printer. The same calculations on a computer of the IBM 1620 class would be prohibitively long and unwieldy.

VI CONCLUSIONS AND RECOMMENDATIONS

(i) Both the equilibrium and non-equilibrium calculations illustrate
the generality and usefulness of data representation by tabulation.
Lagrangian interpolation was found to be advantageous as a method of
table look - up.

(ii) A computer calculation of the efficiency for a system such as
water - acetic acid - MIBK is often the only feasible one. This fact
can result from two occurrences: first,the tie lines may be so flat
that large inaccuracies may be promoted by small experimental errors
in concentration measurements; secondly, when the operating point is
well removed from the diagram, considerable inaccuracy again results
from the graphical calculation.

(iii) By solving the initial problem of simulation, data representa-
tion, a means of improving the assumption of linear relationships for
equilibrium concentrations was found. This method has proven useful
in the transient model.

(iv) The equilibrium stage calculation illustrates the computational
usefulness of a logical sequential search. The method is easy to
program and allows prediction of accuracy while ensuring that the cal-
culation will stop.

(v) While difficulties are encountered by using experimental extremes,
this is more than offset by the information gained by making the cal-

culations work under these limiting physical conditions. For example,
completely different behaviour was found for the arbitrary stage repre-
sentation depending upon whether or not a high flow ratio and high
agitator r.p.m. were used.

(vi) At present it appears that the usefulness of any simulation is
governed by the closeness of fit to the final raffinate and extract
concentrations as well as the degree of reproducibility of the experi-
mental response curves by the computer model. However, in any model a
concentration profile related to distance is also calculated. Hence,
as well as the correspondence of the product concentrations the criterion
of model fit should be based partially on the correspondence of the inter-
nal profile. While experimental measurement of these internal concentra-
tions is difficult, the information would be valuable not only as a
model test but also as a means of indicating the extent of the variation
of $K_E a$ with concentration.

It is therefore, recommended that an experimental column be built
in sections with provision for sampling along the height. This would
allow easy variation of column height and consequently the number of
mixing - settling stages as well as allowing measurement of the concentra-
tion profile. By using single sections a "differential" column could be
constructed. That is, by measuring the concentrations at the end of a
given section, artificial flows with the same concentrations could be
used as inputs to a single stage thereby allowing holdup and coefficient
variations as a function of agitator speed, flow rates and inlet concen-
trations to be more easily isolated and studied.

(vii) The mathematical models were tested by comparing the calculated

and experimental results. Essentially this means that prediction of new conditions can only be made for small perturbations about the original experimental state. Obviously this greatly limits the usefulness of any model. To overcome this liability the form of the concentration and holdup responses, and ultimately the mass - transfer coefficient, as a function of the column variables could be studied by a statistically designed set of experiments. This method would overcome the difficulty of theoretically analyzing and combining the effects of the diverse parameters.

(viii) The present study was limited to introducing step changes in the flow rates. However, the effect of changes in the feed concentration is probably more significant from a practical point of view. Thus, any new apparatus should have provision for some type of manifold system close to the feed inlet to facilitate step changes in concentration while minimizing dead time and diffusion in the connecting tubes.

(ix) A further recommendation concerning equipment and flow measurement in particular concerns better ambient temperature control. While it has been found that the distribution data is relatively insensitive to temperature variations in the neighbourhood of $72 \pm 5^{\circ}F$ (appendix I), it has also been found that the effect of viscosity variation and its subsequent effect on rotameter readings has been significant (appendix II).

(x) An attempt was made with the last experiments to obtain the concentrations of all three components by the use of a gas chromatograph. Unfortunately, for the particular column available, the presence of water obscured the measurement of the ketone. It is suggested that more emphasis be placed on this method of analysis so that the approach to

equilibrium as well as more complete concentration profiles can be obtained. This method of analysis would also aid future work in which models with miscible solvents can be used.

NOTATION

A	diluent of ternary system
a	constant
B	solvent of ternary system
b	constant
C	solute of ternary system
E	extract phase
EA, EB, EC	concentrations of components in extract phase, weight percent
F	feed
FE	flow rate of extract phase, gms/min
FF	flow rate of feed, gms/min
FR	flow rate of raffinate phase, gms/min
FS	flow rate of solvent, gms/min
FN	member of Fibonacci series
$K_E a$	overall mass - transfer coefficient based on extract phase, gms solute/min x cc
k	constant
L_1	fraction of interval at which the first calculation is situated in Fibonacci search
L_f	final range of uncertainty in Fibonacci search
m	constant
N	number of calculations specified in Fibonacci search
NTU	number of transfer units

n	constant
O	operating point
R	raffinate phase
RA, RB, RC	concentrations of components in raffinate phase, weight per cent
r	ratio of molecular weights of nonsolute to solute
S	solvent
T	raffinate phase flow rate, gms solute - free phase/min
t	time, minutes
U	extract phase flow rate, gms solute - free phase/min
V	stage volume, cc
WE	extract phase holdup, gms acid - free phase
WR	raffinate phase holdup, gms acid - free phase
x	concentration of raffinate phase, gms solute/gm solute - free phase
y	concentration of extract phase, gms solute/gm solute - free phase
y*	extract phase concentration which would be in equilibrium with given raffinate phase concentration

Subscripts

1, 2, ... J, ... N	stage number in equilibrium calculation
1, 2, ... i, ... N	stage number in non-equilibrium calculation
F	feed
S	solvent

Greek Letters

Δ difference

ϵ least separation between two calculations in Fibonnaci search for which a difference in the response can be detected

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APPENDIX I DETAILED LITERATURE REVIEW

1.1 System

Sherwood, Evans and Longcor (1) in a paper published in 1939 on extraction in spray and packed columns were the first investigators to use the system acetic acid - water - methyl isobutyl ketone. These workers determined the data experimentally at 25°C. However, no indication was given as to the methods used or the purity of the materials.

Later, in 1941, Othmer, White and Trueger (2) published extensive data on liquid - liquid extraction systems. Included were data obtained at 22°C for the system MIBK - water - acetic acid for both the solubility curve and tie line concentrations.

Two years later Brinsmade and Bliss (3) chose this same system for the study of wetted wall columns. They evaluated equilibrium concentrations at 25°C and 43.3°C. As reasons for their choice of system these authors pointed out that the work of Sherwood (1) was already available and also the distribution coefficient was in the neighbourhood of unity. In their work this latter fact was important since if the individual coefficients (in the additivity of resistance equation) were approximately equal in magnitude the contribution of each to the over-all coefficient would then be significant and not be entirely masked by a very small or a very large value of the distribution coefficient.

In a 1948 publication Scheibel (4) described his mixer - settler

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column which was run using the MIBK - acetic acid - water data published by Othmer et al. (2). Two years later Karr and Scheibel (5) redetermined the distribution data experimentally. Their results were found to compare favourably with those of Sherwood (1) but differed from those of Othmer (2) and Brinsmade (3). The last two sets cover different ranges but appear to be consistent with one another. Karr and Scheibel's (5) data were determined at $28^{\circ}C$ without unusually strict temperature control since Brinsmade and Bliss with results at $25^{\circ}C$ and $43.3^{\circ}C$ found that temperature had little effect for this particular system. Using a sensitive test of distribution data which magnifies discrepancies in the dilute region more than the usual equilibrium curve, namely a plot of the distribution coefficients versus concentration of solute in one phase, this new set of concentrations was found to be very consistent. These authors also found little difference between purified MIBK and MIBK in its original state.

Oldshue and Rushton (6) in a 1952 paper examined the existing data to see whether or not it could be extrapolated to $20^{\circ}C$. They plotted the distribution coefficient at constant water phase acid concentration versus temperature and found the values in the literature to be inconsistent. Their analysis was carried out in the usual manner with titration by NaOH. Equal accuracy was obtained whether the organic phase was titrated in an alcoholic or an aqueous solution. The density measurements were obtained using hydrometers. Their data show that for dilute concentration ranges under 3 wt% acid in the aqueous layer, the equilibrium distribution ratio does not change appreciably over the range $68 \pm 5^{\circ}F$. The data agree fairly well with that of

Scheibel (5) and Sherwood (1).

The most recently published data are that of Karr and Scheibel (7). Densities were determined with a pycnometer and concentrations by titration. This data, which were determined at 25°C, is consistent with the previous work at 28°C by Karr and Scheibel (5). Thus the negligible effect of temperature over limited ranges is again corroborated.

1.1.1 Selection of Data

Most emphasis was placed on the work of Karr and Scheibel (7,5) and no emphasis on that of Brinsmade and Bliss (3) for the equilibrium or tie line concentrations. Solubility data were abstracted from Othmer et al. (2) and Sherwood et al. (3). Graphs were plotted of EC versus RC for the distribution data and EB versus EC for the organic phase and RA versus RC for the aqueous phase. Some minor smoothing of the data was carried out and some extra points added to fill in large gaps on the curve. The values used in all calculations are given in Table 1.

The system was used with the ketone as the dispersed extractant and the water - acetic acid as feed. Scheibel (5,7) reported that this combination produced the most efficient extraction. This contrasts with Moorhead's (8) findings that operation with the ketone phase continuous and extraction from ketone to water was the most efficient of the four combinations for a packed column. This difference illustrates the effect that the mechanics of the extraction process have on the choice of system and method of operation.

1.2 Scheibel Column

A design for a mixer - settler extraction column was published
by Scheibel (4) in 1948. The column consists of alternate calming and
mixing sections with the calming section acting as an entrainment sep-
arator for the two liquids. The heavier liquid flows downward through
the column countercurrent to the lighter phase. The phases are brought
into intimate contact in the mixing sections before flowing into the
packed sections. The countercurrent flow in the packing produces addi-
tional extraction since it is carried out under favorable conditions,
namely that the initial flow into the packing is very highly dispersed.
Thus by considering a stage as composed of a single mixing and calming
section the efficiency might be expected to be better than one theor-
etical stage. However, without complete separation in the packed sec-
tion, the efficiency of the stage is limited by the entrainment of
solvents.

For this column it was found that lower efficiencies were ob-
tained if the mixing chamber volume was increased while leaving the
agitator r.p.m. at a constant value. This led to the conclusion that
the smallest mixing volume is preferable since it gives the lowest power
input and also decreases the overall height of a stage without appre-
ciably affecting the efficiency. In choosing an optimum packing height
it was necessary to balance the height of the section versus the diameter
of the column. That is, the throughput of the column increased with greater
free space but with the greater voidage a correspondingly higher packed
section was required for separation. Since solvents vary in their
difficulty of separation it is obvious that the optimum packing height

must be a function of the solvents. However, unlike packed columns, the efficiency does not decrease with height since channeling is eliminated by agitation.

Performance data for a one inch column are given for a variety of systems including water, acetic acid, MIBK. Efficiencies of over 100% were obtained but at the expense of large settling sections.

In a later paper Scheibel and Karr (5) present performance data for a three stage, twelve inch diameter column operated with four different systems, including water - acetic acid - MIBK. These authors point out that flooding can only be determined within limits and that the theoretical flooding condition is that in which a differential increase in any of the variables causes the dispersed solvent to continuously accumulate in the column. Thus, if conditions are close to flooding, this accumulation is slow and a long period of time would be required for it to become apparent.

Several definite conclusions were stated by these authors. It was found for all cases that the stage efficiency of the column increases with agitator speed to a maximum, then levels off, and if flooding is not produced, decreases. The reason for the decrease is the inability of the packing to break the very fine dispersion produced by excessive agitation. The range of speeds giving maximum efficiency varies with the properties of the solvents and is generally longer for the more readily separable solvent phases. The stage efficiency, at a constant r.p.m., also increases with throughput to a maximum and then levels off until flooding occurs. This behaviour results because the dispersion in the mixing section increased with throughput at the lower flows but

at the higher flows the dispersion appeared to decrease because the quantity of liquid passing through the mixing section was too large to be completely dispersed by the agitation provided.

From their performance curves for the different types of operation and different systems, these workers concluded that the optimum operating conditions differ depending on the direction of diffusion and on which phase is dispersed. The performance appeared better when extracting the solute from the aqueous phase into the organic solvent than in the reverse direction. Also, the dispersion of water in solvent generally required a higher agitator speed for the same efficiency. A qualitative description of the effect of the packing on stage efficiency was also given. It was reported that the less dense packing would have a greater liquid capacity but a larger height would be required for optimum efficiency. This confirms the findings of the earlier paper.

In order to further refine the knowledge of the extraction mechanism in the mixer - settler column, Karr and Scheibel (7) carried out detailed work on the efficiency of the mixing section alone. They attempted to correlate the important variables affecting mass transfer between immiscible liquid flows in an agitated chamber. Over-all mass - transfer coefficients for three different systems were correlated by employing activity as the driving force. A ratio of density difference to interfacial tension between phases, all to the 1.5 power, was used to account for the effect of physical properties on the over-all coefficient. However, the tension used was that of the equilibrium solutions whereas in the actual column, the two phases in the mixing section were not at equilibrium. The over-all coefficients were found to

be independent of the flow rate of the continuous phase and of the discontinuous phase below a critical flow rate but proportional to the flow rate of the discontinuous phase above the critical flow rate.

When the light phase was dispersed the mass - transfer coefficient was found to be proportional to the 4.0 power of the agitator speed and the 3.0 power of the agitator diameter independent of the direction of solute transfer. When the heavy phase was dispersed, the coefficient was found to be proportional to the 3.0 power of the agitator speed and the 2.7 power of the diameter. When the light organic phase was both the dispersed phase and the extractant, exceptionally high mass - transfer coefficients and holdups were obtained. These were attributed to high resistance to coalescence of the drops in this type of operation. Experimentally it was found that for the case MIBK dispersed and extractant, the dispersion was much finer at a given agitator speed than for the case of ketone dispersed but water used as the extractant. Also the holdup for the first method was found to be about three times that of the second at the same r.p.m. and flow rate. Thus, when mass transfer is into dispersed ketone, the tendency for drops to coalesce is much less than when mass transfer is from the drop into the continuous phase. However, no significant difference in the mass - transfer coefficient and holdup for the two directions of mass transfer when water was the dispersed phase was noted.

A further analysis of this type of column was carried out by Honekamp and Burkhart (9). This paper presents an analysis of the role of the packing in a Scheibel column. It was found experimentally that the drop size in a Scheibel extractor is determined by the drop size in

the mixing sections with very little change in size taking place in five inches of packing. Also, these authors concluded that the behaviour of a four - stage Scheibel extractor at constant stirrer speed with respect to drop size and holdup closely parallels a packed column. The great effect of the packing upon the transfer of solute is indicated by the fact that 25 to 50% of the extraction, depending upon the operating conditions, took place in the packing of a four - stage, 3 - inch diameter column with the system water, acetic acid, MIBK. In the normal operating range, the mixers increased the transfer area and decreased the concentration gradient in the packed sections. The effect of the increased transfer area was usually less than the effect of the decreased gradient, resulting in an overall decrease in the packing efficiency with increased stirrer speed.

1.3 Transient Models

Many methods have been used to formulate equations representing transient behaviour of continuous countercurrent contactors. One of the most complete discussions of transient behaviour in both packed and plate columns was presented by Marshall and Pigford (10). Their approach consisted of writing partial differential equations for a material balance over a differential element, transforming variables, and then carrying out a Laplace transformation. However, the ordinary differential equation formed by such a method can be solved generally in only simple cases.

Another analysis of diffusional countercurrent was made by Bowman and Briant (11) and was extended by Jaswon and Smith (12). These authors wrote partial differential equations to describe the column behaviour

and then transformed variables by introducing new independent variables for time and height. This change produced a very simple set of partial differential equations when a linear equilibrium relationship was assumed:

$$\frac{\partial x}{\partial \alpha} = -\frac{\partial y}{\partial \beta} = y - x$$

where α and β are the transformed variables and are related in a complex fashion to height and time. These equations were solved to produce equations which were the product of three functions: an Euler function, a Bessel function and an exponential function. The exponential function, while typical for transient processes, is only valid for a completely mixed system.

However, an important observation in both papers is that the boundary conditions required are complex. If a step change is made in the concentration of the heavy phase, then a discontinuity will exist in this stream as it flows down the column. As the light phase hits this discontinuity, the concentration versus time function in the light phase remains continuous, but the first derivative develops a discontinuity. If the light and heavy phases are physically connected at the bottom of the column, the light phase going up will develop a concentration discontinuity. At the top the discontinuity will be again reflected back down the column. To correctly solve the differential equations, the boundary conditions must be formulated so as to incorporate these discontinuities. The change in independent variables then allows the correct conditions to be applied.

Marshall and Pigford (10) also outlined a transient formulation for stagewise extraction and absorption. These authors generated a set

of ordinary differential equations by making a material balance around each stage. A finite series of exponential terms was eventually obtained for the solution.

Biery and Boylan (13) in 1963 presented detailed work on the transient startup behaviour of a pulsed extraction column. These authors attempted to mathematically clarify the time required to reach steady - state after an upset by comparing the transient response curves of theoretical models with those of actual experiments. Ordinary differential equations describing the interphase mass transfer were obtained by forming transient material balances over finite sections of the column as well as by reducing partial differential equations by finite difference techniques.

Most of the models tried involved stagewise nonequilibrium representations. The degree of mixing in each phase was accounted for by various means such as the assumption of ideal mixing or the assumption that longitudinal concentration gradients were present. For this latter case, the average concentrations of the inlet and outlet flows of a stage were used to approximate the driving force within a stage. Further simplifications were made by assuming that the driving force within the stage could be represented by the driving force above or below the stage. These workers divided the column into an arbitrary number of sections and found that the experimentally determined mass - transfer coefficient was approached by the coefficient used in the model only when the number of stages was large. They also found that computation time was long when the equations were used with large $K_E a$ values. No explanation was given for these two occurrences.

Biery concluded from his work that the stagewise representation gave better stability than was the case when the partial differential equations were used. While most models could be made to reproduce the experimental curves relatively closely, some methods produced instability in the initial delay. No details of the integration step size or the effect on stability with an increasing number of equations were discussed.

These authors also concluded that since the models did not include a longitudinal diffusion term, the experimental curves tended to have shorter dead time periods than would be predicted by the plug flow assumption. However, they stated that since the simulation without the added complexity of the longitudinal diffusion was reasonably good, the models would be adequate for many computer applications.

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APPENDIX II EXPERIMENTAL PROCEDURE

2.1 Operating Procedure

Feed solutions were first mixed on a volume basis to produce a given weight per cent of acetic acid. That is, the desired weight per cent could be closely approximated by volumetric measurement since the density of acetic acid is about 1.05 as opposed to 1.00 for water at temperatures in the region of $23^{\circ}C$. For all except the last two runs, 13 and 14, pure MIBK was used and the feed was kept solvent free. However, it was found from the equilibrium stage calculations that the assumption of immiscible solvents for the transient model did not hold very well under these conditions. Consequently, in these last two experiments the feed was saturated with MIBK and the MIBK with water. Once the required solutions had been prepared, they were loaded by means of a vaccuum system into the overhead feed tanks. If the column had already been filled with the continuous phase, the feed tanks, at flows of about 50 ml/min, contained enough for a run of approximately 2 to 2.5 hours duration or about the time to reach steady - state conditions twice.

Before beginning a run, the glass piping usually had to be taken apart and the joints regreased. This was necessary because the solvent MIBK would dissolve the silicone stopcock grease over a period of about two hours.

The column was then filled with the feed solution and the

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agitator started and set at the desired speed as determined by a stroboscope. It was found that a tachometer tended to reduce the motor speed by means of the extra friction. Next, both flows were started and by means of needle valves set at the desired rotameter readings. The rotameters were calibrated before and after every run by means of a by-pass valve which allowed the flows to be collected in graduated cylinders and timed.

Once the dispersed phase was present throughout the column, the raffinate overflow bulb was adjusted to set the upper interface at the 870 ml. mark. The column volume was calibrated by adding known volumes and marking the levels on a strip of tape which ran the length of the column. The level of 870 was chosen because the extract overflow occurred at 920 and this 50 mls. allowed an element of safety when a step change was introduced in the feed flow rate. If a smaller phase holdup at the top of the column were used then there would be a danger of displacing some of the continuous phase out of the extract overflow when the flow upset occurred.

Having now set all variables to the desired conditions, the column was run until its volume had been displaced five times. This number had been previously determined by sampling every ten minutes and analyzing to see when the concentrations no longer changed. By using column displacement as the criterion, the relative flow rates are automatically accounted for. The total volume collected was measured in a large graduated cylinder.

After five displacements, the feed, solvent, extract and raffinate were sampled by collecting approximately 200 cc in erlenmeyer flasks.

After another column displacement took place, the raffinate and extract were again sampled. Throughout the run and at the end, the agitator r.p.m. was checked to ensure constancy. Generally, the variation was no more than 5 r.p.m. at, for example, 400 over a three hour span.

For a transient run, the timer would be started as the feed flow was suddenly increased. An effort was made to maintain the upper interface level at the same setting. The raffinate was then sampled on the even minutes and the extract on the odd. Since samples representative of points in time were desired, the samples were collected in small test tubes of approximately 10 cc. volumn. However, since these samples were not large enough to allow a density measurement by displacement, larger samples were collected as well over a two minute period at intervals of six minutes. By this means a graph of density versus time could be plotted and subsequently used to find the densities of the small transient samples which were collected in ten seconds or less. Sampling was again continued until five volume displacements had occurred.

At both the initial and final steady - state the upper and lower interface levels were recorded. Also the raffinate and extract flows were measured at both points by timed collections in graduated cylinders.

Having now reached the final steady - state, the column flows were quickly stopped and the phases allowed to separate inside the column so that the new interface could be measured. Thus, by knowing the volumes of extract which had coalesced before and after the flows were halted, an estimate could be obtained for the dispersed phase holdup.

One of the biggest difficulties in the experimental operation was controlling the feed and solvent flow rates. Scheibel (4) reported

that the ball float rotameters appeared to be somewhat sensitive to changes in viscosity resulting from ambient temperature changes. Compounding this difficulty is the fact that the feed tanks do not supply a constant head but in fact as the tank empties the pressure drops about one foot of water in twelve. Also the needle valves were extremely difficult to regulate. The result of these difficulties was that the flowmeters had to be adjusted about once every one or two minutes and the feed and solvent flows could not be kept as constant as desired for good material balances.

2.2 Analytical Procedure

In order to obtain concentrations as weight per cents, the normality and density of the samples are required. The density was obtained by weighing a glass bob immersed to the same degree in water and in the sample solution as well as weighing it hanging freely in air. In order to obtain the density a sample size of about 65 cc was required in order to immerse the bob in the solution which was contained in a glass cylinder.

The concentration was obtained by titrating a pipetted 5 cc aliquot with 0.1 N NaOH using phenolphthalein as the indicator. Rapid agitation was required when the organic phase was titrated with the aqueous sodium hydroxide.

2.3 Chromatographic Analysis

As shown in appendix III, the errors involved in the conventional analysis could be large enough to encourage other methods of analysis.

Also, for the transient runs it is imperative to take point samples and thus a method of analysis is required which will provide concentration as a weight per cent while operating with small samples. A further advantage is that by finding the proper chromatograph column the concentration of all three components can be determined.

A standard Beckman column (No. 70169) was used. The column was six feet long and consisted of carbowax on a teflon support.

Chromatographic analysis of the system water - acetic acid - MIBK proved to be very difficult. The water peak tailed off quite badly and made the measurement of the ketone impossible. If the flow rate was reduced to separate these two peaks then the resolution time of the acetic acid became very long (about 25 minutes) and as a consequence the peak became very low and broad thus providing poor accuracy. Therefore, the column was run at a high flow rate and maximum temperature with only the acetic acid being quantitatively measured.

The particular conditions used were as follows:

> chart speed = 1" / min
>
> pressure   = 45.7 p.s.i.
>
> current   = 268.5 ma.
>
> sample size = 5 μL

These conditions and along with an attenuation of 100 gave peak heights for standard acid samples of 80 divisions. The three component samples, using an attenuation of 20, produced peak heights in the range of 40 divisions and a retention time of about ten minutes.

It was found that peak height measurement did not give reproducible concentrations. Other methods such as one half the base times

the height were of no value since the curve was biased in one direction instead of being symmetrical. Therefore, manual integration was carried out to obtain the concentrations of the samples; that is, the area under the curve, which is proportional to the amount of the acid present in sample, was obtained by counting the squares enclosed by the base line and the chromatograph curve.

Since the operating conditions could not be held absolutely constant, it was necessary to run standards periodically. Perhaps the most important change concerns the flow rate variation. It was found that sensitive flow measurements for the carrier gas, helium, were required in order to determine flow constancy since the pressure gauge on the chromatograph was not very accurate for small changes.

Because of these variations in operating conditions as well as the difficulty of getting absolutely reproducible injection volumes and injection times, the curves varied in broadness and thus in peak height as well. However, the peak area, which should be independent of curve shape, when calculated for three injections of the same solution was found to have variations in the order of 5%.

The net outcome of this method was that the analysis took longer, only the acid could be determined as was the case for analysis by titration, and the accuracy was very rarely much better than that obtained for titration. Also, this method still required density measurements to be independently made since all three components could not be resolved. However, the technique may still be applicable if a better column can be found which will resolve the components and if a better flow indicator for helium is used. If total resolution were possible

then sample volume and injection time would be unimportant providing the sample was representative of the whole solution. That is, weight per cent could be calculated directly from the areas under the three separate curves.

APPENDIX III   RESULTS AND SAMPLE CALCULATIONS

3.1 Experimental Results

       The following Table 8 gives the operating conditions, the
measured parameters, and the calculated efficiencies and material
balances for the experimental runs.

3.2 Equilibrium Stage Calculation

       Table 9 illustrates the print - out obtained from the equil-
ibrium stage calculation for Run 13.   The intermediate flows and
concentrations are used in the calculation of the parameters of the
transient model.

3.3 Error Analysis of Experimental Measurements

       In order to have a specific example to illustrate the errors
and calculations, the results of Run 13 will be used in this section
as well as in section 3.4.

3.3.1 Weight Per Cent: A particular set of solutions from Run 13
will be used to exemplify the calculations and to determine the
relative errors.

   (i) Density: The density is calculated from the following
equation:

Run Number	Agitator r.p.m.	Material Balances		Efficiency		Stream	Concentrations Wt. %			Flows Ml./Min.	Density Gm./Ml.
		Total	Acid	$E_1 - R_N$	$R_N - E_1$		A	B	C		
2	530	2.91%	-8.97%	48.91	38.61	E	5.86	83.71	10.43	0.831	66.70
						R	91.56	2.14	6.20	1.005	33.30
						S	0.00	100.00	0.00	0.801	64.50
						F	81.93	0.00	18.07	1.023	39.00
6	240	4.59	0.82	37.04	35.68	E	5.65	84.32	10.03	0.833	54.30
						R	91.01	2.19	6.80	1.007	30.00
						S	0.00	100.00	0.00	0.801	52.90
						F	81.89	0.00	18.11	1.025	35.80
7	240	7.41	6.84	41.78	42.58	E	7.00	80.29	12.71	0.843	55.50
						R	87.83	2.51	9.66	1.007	53.00
						S	0.00	100.00	0.00	0.801	52.90
						F	81.89	0.00	18.11	1.025	64.20
8A	390	2.05	-4.37	46.76	38.80	E	5.87	83.68	10.45	0.835	55.00
						R	91.44	2.16	6.40	1.005	27.30
						S	0.00	100.00	0.00	0.801	49.70
						F	82.10	0.00	17.90	1.023	34.30
8B	240	3.66	0.91	37.92	35.84	E	5.58	84.54	9.88	0.833	52.00
						R	91.07	2.19	6.74	1.005	28.70
						S	0.00	100.00	0.00	0.801	49.70
						F	82.10	0.00	17.90	1.023	34.30
8C	240	2.12	1.62	44.34	46.07	E	6.93	80.47	12.60	0.841	54.60
						R	87.95	2.50	9.55	1.008	53.30
						S	0.00	100.00	0.00	0.801	49.70
						F	82.10	0.00	17.90	1.023	60.60

TABLE 8: EXPERIMENTAL RESULTS

9	580	0.94	0.71	67.67	58.30	E R S F	9.24 80.02 0.00 79.70	74.01 3.43 100.00 0.00	16.75 16.55 0.00 20.30	0.860 1.019 0.802 1.030	18.77 58.31 17.55 60.39
10	580	2.57	3.02	55.03	60.85	E R S F	12.61 75.58 0.00 74.43	65.16 4.11 100.00 0.00	22.23 20.31 0.00 25.57	0.882 1.026 0.804 1.035	20.00 55.56 17.55 60.39
11	580	-2.21	-3.15	53.18	49.23	E R S F	6.08 85.33 0.00 85.73	83.03 2.75 100.00 0.00	10.89 11.92 0.00 14.27	0.834 1.011 0.798 0.016	17.50 61.75 17.55 60.39
12	580	-4.38	-6.82	59.61	38.71	E R S F	4.23 89.21 0.00 91.20	88.87 2.36 100.00 0.00	6.90 8.43 0.00 9.80	0.822 1.002 0.795 1.010	16.67 64.40 17.55 60.39
13	460	-1.08	0.10	35.40	37.64	E R S F	6.61 88.80 2.30 76.28	81.37 2.41 97.70 4.00	12.02 8.79 0.00 19.72	0.836 1.008 0.798 0.999	43.80 30.00 38.00 35.90
14	460	-0.96	1.16	37.98	43.96	E R S F	7.69 86.43 2.30 76.28	78.35 2.64 97.70 4.00	13.96 10.93 0.00 19.72	0.842 1.011 0.798 0.999	46.50 45.10 38.00 53.70

TABLE 8: EXPERIMENTAL RESULTS (Continued)

TABLE 9: EQUILIBRIUM STAGE CALCULATION

LIQUID-LIQUID EXTRACTION EFFICIENCY CALCULATION
STEADY STATE

SYSTEM = WATER - ACETIC ACID - MIBK

A - WATER
B - MIBK
C - ACETIC ACID

RUN NO. 13   RPM = 460

	A	B	C	DENSITY-GM/ML	FLOW-ML/MIN
EN	6.609	81.374	12.017	0.836	43.800
R1	88.804	2.406	8.790	1.008	30.000
S	2.300	97.700	0.	0.798	38.000
F	76.284	4.000	19.716	0.999	35.900

MATERIAL BALANCES

TOTAL OUT = 66.891   TOTAL IN = 66.177   BALANCE = -1.08
HAC OUT   = 7.062   HAC IN   = 7.069   BALANCE =   0.10

CALCULATION PROCEEDS FROM BOTTOM

CONCENTRATIONS-WT PER CENT						FLOWS-GM/MIN							
RA	RB	RC	EA	EB	EC	FR	FE	FRA	FRB	FRC	FEA	FEB	FEC
88.804	2.406	8.790	3.987	89.840	6.173	30.252	33.307	26.865	0.728	2.659	1.328	29.923	2.056
82.729	3.082	14.189	6.120	82.896	10.985	33.235	36.491	27.495	1.024	4.716	2.233	30.249	4.008
77.988	3.708	18.304	8.221	76.795	14.984	36.419		28.402	1.351	6.666			

EFFICIENCY = 37.636   NUMBER OF THEORETICAL STAGES = 2.258

LIQUID-LIQUID EXTRACTION EFFICIENCY CALCULATION
STEADY STATE

SYSTEM = WATER - ACETIC ACID - MIBK

A - WATER
B - MIBK
C - ACETIC ACID

RUN NO. 13   RPM = 460

	A	B	C	DENSITY-GM/ML	FLOW-ML/MIN
E1	6.609	81.374	12.017	0.836	43.800
RN	88.804	2.406	8.790	1.008	30.000
S	2.300	97.700	0.	0.798	38.000
F	76.284	4.000	19.716	0.999	35.900

MATERIAL BALANCES

TOTAL OUT = 66.891   TOTAL IN = 66.177   BALANCE = -1.08
HAC OUT   = 7.062   HAC IN   = 7.069   BALANCE =   0.10

CALCULATION PROCEEDS FROM TOP

CONCENTRATIONS-WT PER CENT						FLOWS-GM/MIN							
EA	EB	EC	RA	RB	RC	FE	FR	FEA	FEB	FEC	FRA	FRB	FRC
6.609	81.374	12.017	81.512	3.239	15.249	36.639	32.290	2.422	29.814	4.403	26.320	1.046	4.924
4.206	88.964	6.823	87.909	2.500	9.591	33.075	29.298	1.391	29.425	2.259	25.755	0.733	2.810
2.747	95.273	1.980	94.828	2.036	3.136	30.083		0.826	28.661	0.596			

EFFICIENCY = 35.401   NUMBER OF THEORETICAL STAGES = 2.124

$$\text{Density} = \frac{\text{wt. of bob in air} - \text{wt. in solution}}{\text{wt. in air} - \text{wt. in water}} \qquad (1)$$

From repeated measurements the following measurements and error estimates were obtained:

Weight of bob in air   = 5.6015 ± 0.002 gms.

Weight of bob in water   = 3.0859 ± 0.002 gms.

Weight of bob in raffinate = 3.0647 ± 0.003 gms.

Weight of bob in extract   = 3.4973 ± 0.003 gms.

Therefore $\rho_R = 2.5368 \pm 0.005 / 2.5156 \pm 0.004$

$= 1.0084 \pm 0.356\%$

$= 1.0084 \pm 0.0036$

Similarly $\rho_E = 0.8365 \pm 0.497\%$

$= 0.8365 \pm 0.0042$

(ii) Concentration: The concentration is calculated from the following equation:

$$\text{Concentration} = \frac{\text{titrant volume} \times N_{NaOH}}{\text{sample volume}} \qquad (2)$$

Titrant volume for raffinate = 7.38 ± 0.01 mls.

Titrant volume for extract = 8.37 ± 0.01 mls.

The Normality of the NaOH was 1.000 ± 0.002. The solution was prepared from a commercial concentrate guaranteed to ± 0.001 N.

The sample volume used for both solutions was 5.00 mls. However, because of the nature of the organic solvent, normal wetting and drainage, of the pipette did not occur. Consequently, it was estimated that the extract phase had an absolute error of about $\pm$ a drop i.e. ± 0.04 mls.

Since the raffinate had a higher concentration of water, the wetting characteristics were better and the error was estimated to be approximately $\pm$ 0.03 mls.

Therefore $C_R = \dfrac{7.38 \pm 0.01 \times 1.000 \pm 0.002}{5.00 \pm 0.03}$

$= 1.476 \pm 0.936\%$ N

Similarly $C_E = \dfrac{8.37 \pm 0.01 \times 1.000 \pm 0.002}{5.00 \pm 0.04}$

$= 1.674 \pm 1.119\%$ N

(iii) Weight Per Cent: The weight per cent is calculated from equation (3):

$$\text{Weight } \% = \frac{N_{solution} \times MW_{HAC}}{1000 \times \rho_{solution}} \times 100\% \tag{3}$$

where the molecular weight of acetic acid is 60.05

Hence, using the errors calculated in the previous two sections, the weight percentages and the errors can be calculated.

$\text{Wt.\% R} = \dfrac{1.476 \pm 0.936\% \times 60.05}{1000 \times 1.0084 \pm 0.356\%} \times 100\%$

$= 8.790 \pm 1.29\%$

$= 8.790 \pm 0.113$

$\text{Wt.\% E} = \dfrac{1.674 \pm 1.119\% \times 60.05}{1000 \times 0.8365 \pm 0.497\%} \times 100\%$

$= 12.017 \pm 1.616\%$

$= 12.017 \pm 0.194$

For the transient analysis, these concentrations are converted into the units gms of acid/gm of acid free phase.

Thus $x = \dfrac{wt.\% R}{100 - wt.\% R}$

$$\text{(4)}$$

$y = \dfrac{wt.\% E}{100 - wt.\% E}$

From the above values

$x = 0.0963 \pm 2.58\%$

$\quad = 0.963 \pm 0.0025$

$y = 0.1370 \pm 3.34\%$

$\quad = 0.1370 \pm 0.0045$

3.3.2 Volume Measurements

(i) Flow Rates: The flows were measured by collecting the solutions in a graduated cylinder over a known time interval. Usually three or more measurements were made for each stream and in general the error was around $\pm$ 1 ml./min. This error, which is relatively independent of flow rate magnitude, is due to small errors in timing and errors in reading the meniscus level in the cylinder.

For example, for Run 13, the feed flow was estimated as 71.9 and 71.5 mls. in two minutes while the extract flow was estimated as 86.8, 86.0, 85.1 and 84.6 mls. per two minutes.

(ii) Column Volumes: The column overflow occurred at the 925 ml. mark while the upper interface was controlled at 870 ml. At the bottom of the column the dispersed phase was not present below the 165 ml. mark. When phase separation was allowed the new interface occurred at the 830

ml. level.

Since volume markings were made at 25 ml. intervals all readings should be accurate to better than ± 5 ml.

From these measurements the holdups within the column can be calculated. For example,

Dispersed phase holdup = (925 - 830) - (925 - 870)

$$= \quad 95 \quad - \quad 45 \; = 50 \; mls.$$

3.4 Calculation of Parameters for the Transient Model

Figure 13(a) shows a block diagram representation of the column. Now the experimental measurements must be converted into units suitable for the transient model. Figure 13(b) shows the values used for this model. The calculations which are carried out in order to obtain the numbers shown in 13(b) are outlined next.

(i) Concentrations: The concentrations are converted from weight per cent to grams of solute per gram of solute free phase.

Hence: $x_1 = \frac{19.72}{80.28} = 0.246$

$$x_N = \frac{8.79}{91.21} = 0.0963$$

$$y_2 = \frac{12.02}{87.98} = 0.137$$

$$y_S = \frac{0.00}{100.0} = 0.0$$

(ii) Flows: The model incorporates the assumption of immiscible solvents, which for this particular system is not strictly correct.

(a)   Experimental Values

FC = 19.716   RC = 8.790
FF = 35.9   FR = 30.0
 ρ = 0.9987 ρ = 1.0084

                        11.481%
                        665 mls.

                        10.185%
                        40 mls.

EC = 12.017   SC = 0.000
FE = 43.8   FS = 38.0
 ρ = 0.8365 ρ = 0.798

(b)   Transient Model

X_1 = 0.246 X_N = 0.0963
T = 28.2   WR = 593   T = 28.2

                            WE = 26.5

Y_2 = 0.137 Y_s = 0.00
U = 31.3   U = 31.3
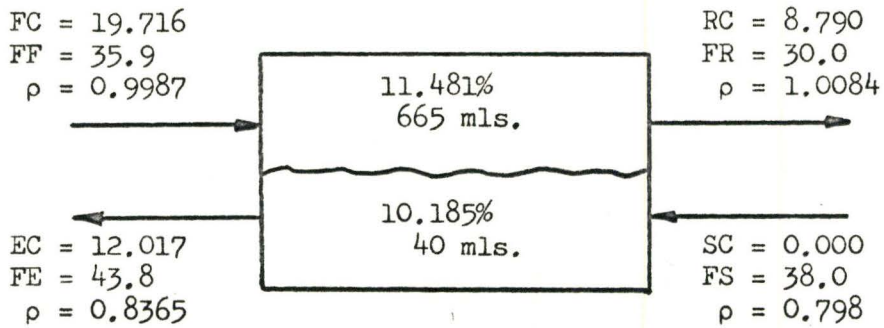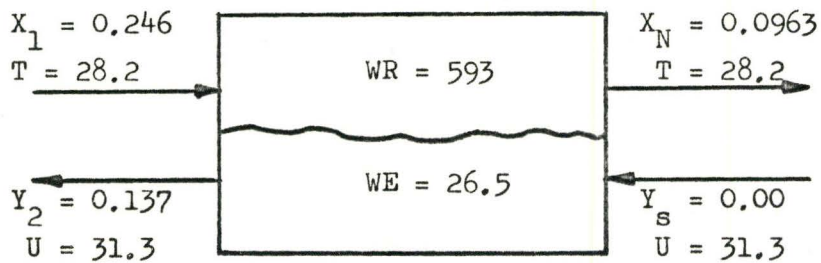
FIGURE 13:   TRANSIENT CALCULATIONS FOR RUN 13

However, in order to make the assumption reasonably accurate, the aqueous phase was initially saturated with ketone and the solvent phase saturated with water. The effect of this technique can be checked by calculating the flows from both the inlet and outlet of a particular phase.

Therefore using the values given in Figure 13(a) the flows can be calculated as follows:

(a) U: From E: $U = FE \cdot \rho_E \cdot \dfrac{(100 - EC)}{100}$ gms. solute - free phase per minute

$$U = 43.8 \times 0.8365 \times \frac{87.98}{100.0}$$

$$= 32.2$$

From S: $U = 38.0 \times 0.798 \times \dfrac{100.0}{100.0}$

$$= 30.4$$

Hence $U_{average} = 31.3$

(b) T: From R: $T = 30.0 \times 10084 \times \dfrac{91.21}{100.0}$

$$= 27.6$$

From F: $T = 35.9 \times 0.9987 \times \dfrac{80.28}{100.0}$

$$= 28.8$$

Hence $T_{average} = 28.2$

(iii) Phase Holdups: Since the total volume and concentration of each phase are known experimentally, the WR and WE of the transient model can be readily calculated.

$WR = 665 \times \dfrac{88.52}{100.0} \times 1.008 = 593$ gms. of solute - free raffinate phase

$WE = 40 \times \frac{89.79}{100.0} \times 0.831 = 26.5$ gms. of solute – free extract phase

(iv) Material Balance: The use of the averaged flows can be checked by comparing the material balance made from the transient parameters with that made using the experimental values.

From the transient model:

Input = $0.246 \times 28.2 = 6.937$ gms. of solute

Output = $0.137 \times 31.3 + 0.0963 \times 28.2$

$= 4.2881 + 2.7157$

$= 7.004$ gms. of solute

This represents an imbalance of 0.9% compared to 0.1% for the results shown in Table 9.

(v) Calculation of $K_E a$ from Experimental Results: In order to estimate the mass – transfer coefficient equation (18) (page 28) must first be evaluated. The first term is obtained from the graphical integration shown in Figure 14. The ends of the operating line represent the experimental concentrations. Interior points were obtained from the equilibrium stage calculations shown in Table 9.

The results of the calculation are:

First term = 2.247

Second term = $\frac{1}{2} \ell n \left(\frac{100 - 12.02}{100 - 0.00} \right) = - 0.0641$

Third term = $\frac{1}{2} \ell n \left(\frac{12.02(0.667) + 100}{100} \right) = 0.0390$

Hence $NTU_{OE} = 2.222$

Now $K_E a = \frac{NTU_{OE} \cdot U}{V}$

$= \frac{2.222 \times 31.8}{705} = 0.101$

85
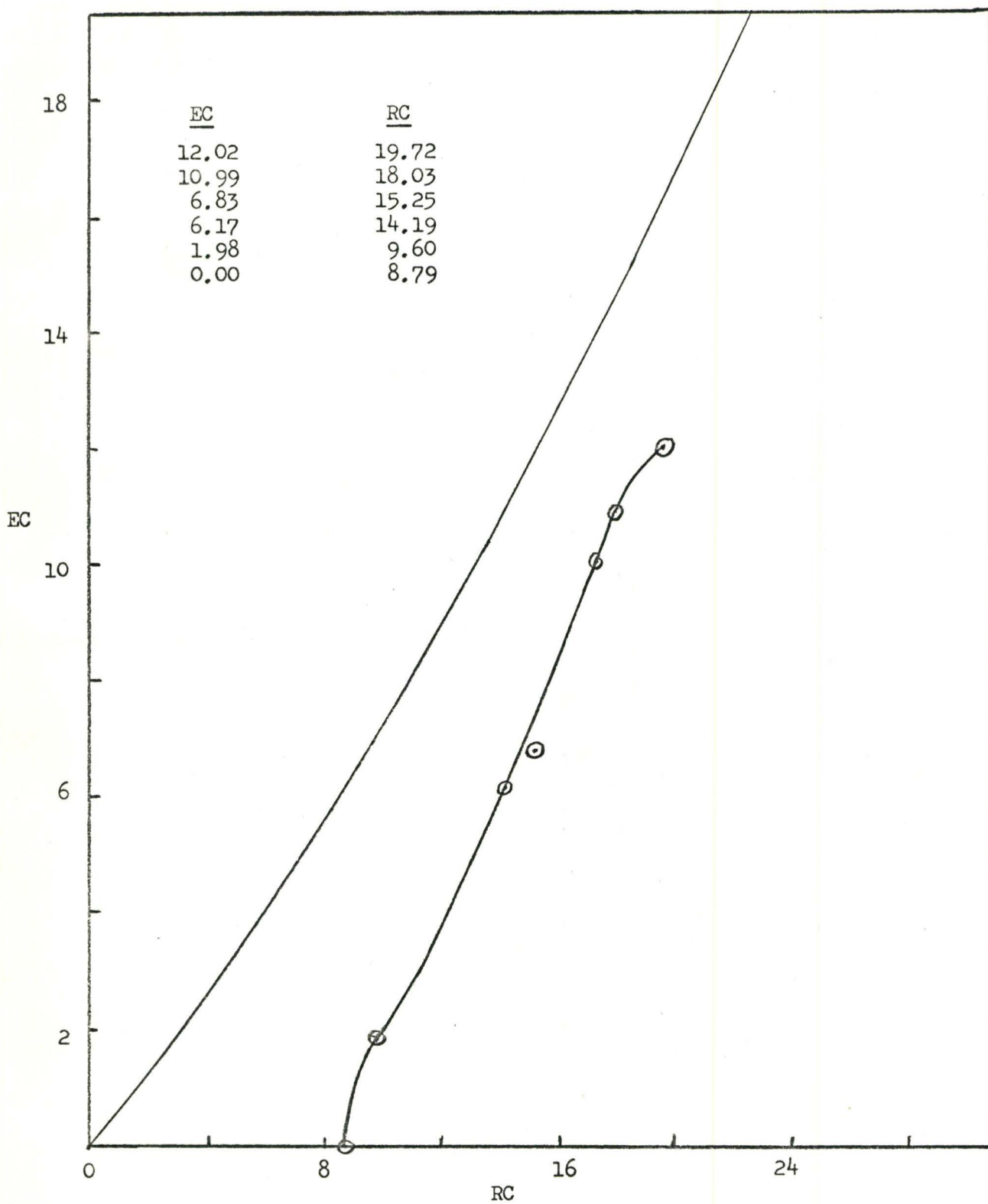
FIGURE 14:   GRAPHICAL EVALUATION OF $K_E a$

(vi) Evaluation of $K_E a$ for Six Stages: The $K_E a$ which would produce the correct total mass transfer was obtained by comparing the predicted steady - state concentrations with the experimental values. The differences were then squared and the minimum value used as the indicator for the correct $K_E a$. The following Table 10 shows the effect of the various $K_E a$ choices upon the closeness of the experimental and theoretical concentrations.

TABLE 10: EVALUATION OF $K_E a$ for SIX STAGES

$K_E a$	Concentrations				(Differences)^2
	X	Difference	Y	Difference	
0.101	0.1096	+0.0133	0.1225	−0.0145	
0.120	0.1036	+0.0073	0 1282	−0.0088	
0.140	0.0984	+0.0021	0.1389	−0.0041	
0.150	0.0963	0.0000	0.1349	−0.0021	441
0.155	0.0953	−0.0010	0.1358	−0.0012	244
0.156	0.0951	−0.0012	0.1360	−0.0010	244
0.157	0.0949	−0.0014	0.1362	−0.0008	260
0.160	0.0943	−0.0020	0.1367	−0.0003	409
Experimental					
	0.0963		0.1370		

3.5 Fibonacci Search Calculation

As an example, assume that it is desirable to find the value of FR_1 for which $|\Delta EC_2|$ is a minimum. Suppose that from preliminary work it is known that FR_1 must lie between 0.0 and 100.0 gms/min. and that ϵ is approximately 0.01 gms./min. Then from equation (14), (15), and (16) in the main body of this report, the following calculations can be made:

$$N_{max} \leq 4.785 \log (\frac{100}{0.1}) - 0.328$$

$$\leq 18.812$$

Hence the maximum number of calculations is 18.

If 11 calculations are used, then

$$L_f = \frac{1}{F_{11}} + \frac{F_9}{F_{11}} \times 0.01 = \frac{1}{144} + \frac{55}{144} \times 0.01$$

$$= 0.0105$$

This means that by using only eleven sequential calculations, the final interval of uncertainty can be reduced to approximately 1% of the original range. If ϵ can be decreased then the limiting fraction of 1/144 is approached.

The location of the initial point is calculated as follows:

$$L_1 = \frac{F_{10}}{F_{11}} + \frac{0.01(-1)^{11}}{F_{11}} = \frac{89}{144} - \frac{0.01}{144} = 0.6181$$

The first calculation is then placed at $FR_1 = 61.81$ while the second is put at 38.19.

Two aspects of this technique should be emphasized: first, the range which is optimized is FR_1 not $|\Delta EC_2|$; second, by choosing the total number of calculations in advance, the program automatically stops at the predetermined accuracy. This search can also be used on discontinuous functions. The following table 10 shows the power of this search. The reduction ratio is the fraction of the original interval remaining after a particular number of experiments or calculations.

TABLE 11:   REDUCTION RATIO FOR SEQUENTIAL FIBONACCI SEARCH

No. of Calculations or Experiments	Reduction Ratio L_o/L_r
0	1
1	1
2	2
3	3
4	5
5	8
6	13
7	21
8	34
9	55
10	89
11	144
12	233
13	377
14	610
15	987
16	1597
17	2584
18	4181
19	6765
20	10946

APPENDIX IV PROGRAM LISTINGS

The following pages present the listings of the programs
used in the various calculations described in this report. Section
4.1.1 lists the equilibrium stage calculation which starts at E_1 and
proceeds to R_N while 4.1.2 list the alternate method which starts at
R_N and moves up to E_1. Section 4.2 reproduces the program which cal-
culates the steady-state concentrations from an N·stage model. Section
4.3 lists the calculation which produces the transient **response** after
starting from a steady - state profile and applying a linear change of
K_Ea over a given number of volume displacements.

4.1.1   EQUILIBRIUM   STAGE   CALCULATION   E(1) TO R(N)


```
C       LIQUID-LIQUID EXTRACTION                                  GARY POLLOCK
C       STEADY STATE EFFICIENCY CALCULATION     -    LAGRANGIAN INTERPOLATION
C                               FIBONACCI SEARCH
C            CALCULATION PROCEEDS FROM TOP TO BOTTOM      E - R
C
C
C       MEMORY RESERVATION
        DIMENSION EQEC(30),EQRC(30),ARA(30),ARB(30),ARC(30)
        DIMENSION BEA(30),BEB(30),BEC(30),EA(30),EB(30),EC(30)
        DIMENSION RA(30),RB(30),RC(30),FE(30),FR(30)
        DIMENSION FRA(30),FRB(30),FRC(30),FEA(30),FEB(30),FEC(30)
        DIMENSION F(25)
        COMMON ACTSG
C
C       SYSTEM DATA
        READ 900,L,M,N
        READ 901,(EQEC(I),EQRC(I),I=1,L)
        READ 902,(ARA(I),ARB(I),ARC(I),I=1,M)
        READ 902,(BEA(I),BEB(I),BEC(I),I=1,N)
        READ 903,ACTSG,LIM
        READ 900,NUM,LIMIT
C
C       FIBONACCI SERIES
        F(1)=1.0
        F(2)=2.0
        DO 5 LLL=3,25
      5 F(LLL)=F(LLL-1)+F(LLL-2)
C
C
C
        DO 100 JJ=1,NUM
C
C       EXPERIMENTAL DATA
        READ 900,NO,LRPM
        READ 905,EC(1),RHOE,FFE1
        READ 905,RNC,RHOR,FFRN
        READ 904,SA,SB,SC,RHOS,FFS
        READ 904,FA,FB,FC,RHOF,FFF
        CALL INTERP(N,BEC,BEA,EC(1),EA(1))
        EB(1)=100.0-EC(1)-EA(1)
        CALL INTERP(M,ARC,ARB,RNC,RNB)
        RNA=100.0-RNB-RNC
C
C       OVERALL MATERIAL BALANCE
        FF=FFF*RHOF
        FS=FFS*RHOS
        FE(1)=FFE1*RHOE
        FRN=FFRN*RHOR
        AA=FF+FS
        BB=FE(1)+FRN
        CC=(AA-BB)/AA*100.0
```

```
      AAC=(FF*FC+FS*SC)/100.0
      BBC=(FE(1)*EC(1)+FRN*RNC)/100.0
      CCC=(AAC-BBC)/AAC*100.0
C
C     HEADINGS
      PRINT 950
      PRINT 951
      PRINT 952
      PRINT 953
      PRINT 954
      PRINT 955
      PRINT 956,NO,LRPM
      PRINT 957
      PRINT 958,EA(1),EB(1),EC(1),RHOE,FFE1
      PRINT 959,RNA,RNB,RNC,RHOR,FFRN
      PRINT 960,SA,SB,SC,RHOS,FFS
      PRINT 961,FA,FB,FC,RHOF,FFF
      PRINT 962
      PRINT 963,BB,AA,CC
      PRINT 964,BBC,AAC,CCC
      PRINT 965
      PRINT 966
      PRINT 967
C
C     EQUILIBRIUM CALCULATION
      J=0
   10 J=J+1
      CALL INTERP(L,EQEC,EQRC,EC(J),RC(J))
      CALL INTERP(M,ARC,ARB,RC(J),RB(J))
      RA(J)=100.0-RC(J)-RB(J)
      IF(RNC.GE.RC(J)) GO TO 70
C
C
C     FIBONACCI SEARCH FOR FLOWS
C
C
C     RANGE MAXIMUM
      X0=(FF*FC-FE(1)*EC(1))/RC(J)
      IF(X0.LT.0.0)   X0=0.0
   13 FE(J+1)=X0+FE(1)-FF
      EA(J+1)=(X0*RA(J)+FE(1)*EA(1)-FF*FA)/FE(J+1)
      IF(EA(J+1).GT.BEA(1).AND.EA(J+1).GT.0.0) GO TO 15
      X0=X0+0.3
      GO TO 13
   15 CALL INTERP(N,BEA,BEC,EA(J+1),EC(J+1))
      CALCC=(X0*RC(J)+FE(1)*EC(1)-FF*FC)/FE(J+1)
      Y0=ABS(EC(J+1)-CALCC)
C
C     RANGE MAXIMUM
      XN=FF+FS
   20 FE(J+1)=XN+FE(1)-FF
      EA(J+1)=(XN*RA(J)+FE(1)*EA(1)-FF*FA)/FE(J+1)
      IF(EA(J+1).LT.BEA(N)) GO TO 25
      XN=XN-1.0
      GO TO 20
```

```
   25 CALL INTERP(N,BEA,BEC,EA(J+1),EC(J+1))
      CALCC=(XN*RC(J)+FE(1)*EC(1)-FF*FC)/FE(J+1)
      YN=ABS(EC(J+1)-CALCC)
C
C     INITIAL PLACEMENT
      S2=(XN-X0)*(F(LIMIT-1)/F(LIMIT))
      X1=XN-S2
      X2=X0+S2
      FE(J+1)=X1+FE(1)-FF
      EA(J+1)=(X1*RA(J)+FE(1)*EA(1)-FF*FA)/FE(J+1)
      CALL INTERP(N,BEA,BEC,EA(J+1),EC(J+1))
      CALCC=(X1*RC(J)+FE(1)*EC(1)-FF*FC)/FE(J+1)
      Y1=ABS(EC(J+1)-CALCC)
      FE(J+1)=X2+FE(1)-FF
      EA(J+1)=(X2*RA(J)+FE(1)*EA(1)-FF*FA)/FE(J+1)
      CALL INTERP(N,BEA,BEC,EA(J+1),EC(J+1))
      CALCC=(X2*RC(J)+FE(1)*EC(1)-FF*FC)/FE(J+1)
      Y2=ABS(EC(J+1)-CALCC)
C
C     SEARCH
      LLIM=LIMIT-2
      DO 61 NOFIB=1,LLIM
      IF(Y1.GE.Y2) GO TO 60
      XN=X2
      YN=Y2
      X2=X1
      Y2=Y1
      X0=X0
      Y0=Y0
      X1=X0+(XN-X2)
      FE(J+1)=X1+FE(1)-FF
      EA(J+1)=(X1*RA(J)+FE(1)*EA(1)-FF*FA)/FE(J+1)
      CALL INTERP(N,BEA,BEC,EA(J+1),EC(J+1))
      CALCC=(X1*RC(J)+FE(1)*EC(1)-FF*FC)/FE(J+1)
      Y1=ABS(EC(J+1)-CALCC)
      IF(X1.LT.X2) GO TO 61
      XX=X1
      YY=Y1
      X1=X2
      Y1=Y2
      X2=XX
      Y2=YY
      GO TO 61
   60 X0=X1
      Y0=Y1
      X1=X2
      Y1=Y2
      XN=XN
      YN=YN
      X2=XN-(X1-X0)
      FE(J+1)=X2+FE(1)-FF
      EA(J+1)=(X2*RA(J)+FE(1)*EA(1)-FF*FA)/FE(J+1)
      CALL INTERP(N,BEA,BEC,EA(J+1),EC(J+1))
      CALCC=(X2*RC(J)+FE(1)*EC(1)-FF*FC)/FE(J+1)
```

```
      Y2=ABS(EC(J+1)-CALCC)
      IF(X1.LT.X2) GO TO 61
      XX=X1
      YY=Y1
      X1=X2
      Y1=Y2
      X2=XX
      Y2=YY
   61 CONTINUE
C
C
C     STAGE MATERIAL BALANCE
      FR(J)=(X1+X2)/2.0
      FE(J+1)=FR(J)+FE(1)-FF
      EA(J+1)=(FR(J)*RA(J)+FE(1)*EA(1)-FF*FA)/FE(J+1)
      CALL INTERP(N,BEA,BEC,EA(J+1),EC(J+1))
      EB(J+1)=100.0-EA(J+1)-EC(J+1)
C
C     PRINT CONCENTRATIONS AND FLOWS
      FRA(J)=FR(J)*RA(J)
      FRB(J)=FR(J)*RB(J)
      FRC(J)=FR(J)*RC(J)
      FEA(J)=FE(J)*EA(J)
      FEB(J)=FE(J)*EB(J)
      FEC(J)=FE(J)*EC(J)
      F1=FE(J)
      F2=FR(J)
      F3=FEA(J)/100.0
      F4=FEB(J)/100.0
      F5=FEC(J)/100.0
      F6=FRA(J)/100.0
      F7=FRB(J)/100.0
      F8=FRC(J)/100.0
      IF(RNC.GE.RC(J)) GO TO 70
      PRINT 968,EA(J),EB(J),EC(J),RA(J),RB(J),RC(J),F1,F2,F3,F4,F5,F6,
     1          F7,F8
      GO TO 71
   70 F1=FE(J)
      F3=FE(J)*EA(J)/100.0
      F4=FE(J)*EB(J)/100.0
      F5=FE(J)*EC(J)/100.0
      PRINT 971,EA(J),EB(J),EC(J),RA(J),RB(J),RC(J),F1,F3,F4,F5
   71 IF(RNC.GE.RC(J)) CALL EFFCY(RNC,RC(J-1),RC(J),J)
      IF(RNC.GE.RC(J)) GO TO 100
      IF(J.LE.LIM) GO TO 10
      PRINT 969,LIM
      PRINT 970
C
C
C
  100 CONTINUE
C
C     FORMAT STATEMENTS
  900 FORMAT(3I4)
```

```
  901 FORMAT(2F6.2)
  902 FORMAT(3F6.2)
  903 FORMAT(F6.1,I3)
  904 FORMAT(5F6.3)
  905 FORMAT(3F6.3)
C
  950 FORMAT(43X,47HLIQUID-LIQUID EXTRACTION EFFICIENCY CALCULATION/)
  951 FORMAT(60X,12HSTEADY STATE///)
  952 FORMAT(48X,36HSYSTEM =  WATER - ACETIC ACID - MIBK//)
  953 FORMAT(61X,9HA - WATER)
  954 FORMAT(61X,8HB - MIBK)
  955 FORMAT(61X,15HC - ACETIC ACID//)
  956 FORMAT(51X,8HRUN NO. I3,10X,5HRPM =I4//)
  957 FORMAT(   6X,22X,1HA,19X,1HB,19X,1HC,13X,13HDENSITY-GM/ML,8X,
     1          11HFLOW-ML/MIN/)
  958 FORMAT(13X,2HE1,F16.3,4F20.3)
  959 FORMAT(13X,2HRN,F16.3,4F20.3)
  960 FORMAT(13X,2HS ,F16.3,4F20.3)
  961 FORMAT(13X,2HF ,F16.3,4F20.3/)
  962 FORMAT(57X,17HMATERIAL BALANCES/)
  963 FORMAT(29X,11HTOTAL OUT =F7.3,10X,10HTOTAL IN =F7.3,11X,9HBALANCE
     1=F7.2)
  964 FORMAT(29X,11HHAC OUT   =F7.3,10X,10HHAC IN   =F7.3,11X,9HBALANCE
     1=F7.2//)
  965 FORMAT(53X,29HCALCULATION PROCEEDS FROM TOP///)
  966 FORMAT(17X,26HCONCENTRATIONS-WT PER CENT,40X,12HFLOWS-GM/MIN/)
  967 FORMAT( 9X,2HEA,6X,2HEB,6X,2HEC,6X,2HRA,6X,2HRB,6X,2HRC,9X,2HFE,
     116X,2HFR,6X,3HFEA,5X,3HFEB,5X,3HFEC,5X,3HFRA,5X,3HFRB,5X,3HFRC//)
  968 FORMAT(5X,6F8.3,3X,8F8.3//)
  969 FORMAT(56X,16HERROR-MORE THAN I3,6HSTAGES///)
  970 FORMAT(1H1)
  971 FORMAT(5X,6F8.3,3X,F8.3,8X,3F8.3//)
C
      STOP
      END



      SUBROUTINE INTERP(JK,X,Y,XA,YA)
      DIMENSION X(30),Y(30)
      YA=0.0
      IF((X(1)-X(2)).GT.0.0) GO TO 804
      DO 805 II=1,JK
      IF((XA-X(II)).LE.0.0) GO TO 806
  805 CONTINUE
  804 DO 809 II=1,JK
      IF((X(II)-XA).LE.0.0) GO TO 806
  809 CONTINUE
  806 IF(II.LE.3) GO TO 807
      IF(II.GE.(JK-2)) GO TO 808
      MM=II-3
      MMM=II+2
      GO TO 810
  807 MM=1
```

```
      MMM=6
      GO TO 810
  808 MM=JK-5
      MMM=JK
  810 DO 801 I=MM,MMM
      PROD=Y(I)
      DO 800 J=MM,MMM
      IF(J.EQ.I) GO TO 800
      PROD=PROD*(XA-X(J))/(X(I)-X(J))
  800 CONTINUE
  801 YA=YA+PROD
      RETURN
      END



      SUBROUTINE EFFCY(A,B,C,J)
      COMMON ACTSG
      FRACT=(A-B)/(C-B)
      Z=J-1
      YY=Z+FRACT
      EFF=100.0*YY/ACTSG
      PRINT 802,EFF,YY
      PRINT 803
  802 FORMAT(33X,12HEFFICIENCY = F7.3,10X,31HNUMBER OF THEORETICAL STAGE
     1S = F6.3/)
  803 FORMAT(1H1)
      RETURN
      END
```

4.1.2 EQUILIBRIUM STAGE CALCULATION   R(N) TO E(1)


```
C       LIQUID-LIQUID EXTRACTION                              GARY POLLOCK
C       STEADY STATE EFFICIENCY CALCULATION    -    LAGRANGIAN INTERPOLATION
C                               FIBONACCI SEARCH
C               CALCULATION PROCEEDS FROM BOTTOM TO TOP    R - E
C
C
C       MEMORY RESERVATION
        DIMENSION EQEC(30),EQRC(30),ARA(30),ARB(30),ARC(30)
        DIMENSION BEA(30),BEB(30),BEC(30),EA(30),EB(30),EC(30)
        DIMENSION RA(30),RB(30),RC(30),FE(30),FR(30)
        DIMENSION FRA(30),FRB(30),FRC(30),FEA(30),FEB(30),FEC(30)
        DIMENSION F(25)
        COMMON ACTSG
C
C       SYSTEM DATA
        READ 900,L,M,N
        READ 901,(EQEC(I),EQRC(I),I=1,L)
        READ 902,(ARA(I),ARB(I),ARC(I),I=1,M)
        READ 902,(BEA(I),BEB(I),BEC(I),I=1,N)
        READ 903,ACTSG,LIM
        READ 900,NUM,LIMIT
C
C       FIBONACCI SERIES
        F(1)=1.0
        F(2)=2.0
        DO 5 LLL=3,25
      5 F(LLL)=F(LLL-1)+F(LLL-2)
C
C
        DO 100 JJ=1,NUM
C
C       EXPERIMENTAL DATA
        READ 900,NO,LRPM
        READ 905, ENC,RHOE,FFEN
        READ 905,RC(1),RHOR,FFR1
        READ 904,SA,SB,SC,RHOS,FFS
        READ 904,FA,FB,FC,RHOF,FFF
        CALL INTERP(N,BEC,BEA,ENC,ENA)
        ENB=100.0-ENC-ENA
        CALL INTERP(M,ARC,ARB,RC(1),RB(1))
        RA(1)=100.0-RB(1)-RC(1)
C
C       OVERALL MATERIAL BALANCE
        FF=FFF*RHOF
        FS=FFS*RHOS
        FEN=FFEN*RHOE
        FR(1)=FFR1*RHOR
        AA=FF+FS
        BB=FEN+FR(1)
        CC=(AA-BB)/AA*100.0
```

```fortran
      AAC=(FF*FC+FS*SC)/100.0
      BBC=(FEN*ENC+FR(1)*RC(1))/100.0
      CCC=(AAC-BBC)/AAC*100.0
C
C     HEADINGS
      PRINT 950
      PRINT 951
      PRINT 952
      PRINT 953
      PRINT 954
      PRINT 955
      PRINT 956,NO,LRPM
      PRINT 957
      PRINT 958,ENA,ENB,ENC,RHOE,FFEN
      PRINT 959,RA(1),RB(1),RC(1),RHOR,FFR1
      PRINT 960,SA,SB,SC,RHOS,FFS
      PRINT 961,FA,FB,FC,RHOF,FFF
      PRINT 962
      PRINT 963,BB,AA,CC
      PRINT 964,BBC,AAC,CCC
      PRINT 965
      PRINT 966
      PRINT 967
C
C     EQUILIBRIUM CALCULATION
      J=0
   10 J=J+1
      CALL INTERP(L,EQRC,EQEC,RC(J),EC(J))
      CALL INTERP(N,BEC,BEA,EC(J),EA(J))
      EB(J)=100.0-EA(J)-EC(J)
      IF(ENC.LE.EC(J)) GO TO 70
C
C
C     FIBONACCI SEARCH FOR FLOWS
C
C     RANGE MINIMUM
      IF(X0.LT.0.0)  X0=0.0
      X0=(FS*SC-FR(1)*RC(1))/EC(J)
   13 FR(J+1)=X0+FR(1)-FS
      RB(J+1)=(X0*EB(J)+FR(1)*RB(1)-FS*SB)/FR(J+1)
      IF(RB(J+1).GT.ARB(1).AND.FR(J+1).GT.0.0) GO TO 15
      X0=X0+0.3
      GO TO 13
   15 CALL INTERP(M,ARB,ARC,RB(J+1),RC(J+1))
      CALCC=(X0*EC(J)+FR(1)*RC(1)-FS*SC)/FR(J+1)
      Y0=ABS(RC(J+1)-CALCC)
C
C     RANGE MAXIMUM
      XN=FF+FS
   20 FR(J+1)=XN+FR(1)-FS
      RB(J+1)=(XN*EB(J)+FR(1)*RB(1)-FS*SB)/FR(J+1)
      IF(RB(J+1).LT.ARB(M)) GO TO 25
      XN=XN-1.0
      GO TO 20
```

```
   25 CALL INTERP(M,ARB,ARC,RB(J+1),RC(J+1))
      CALCC=(XN*EC(J)+FR(1)*RC(1)-FS*SC)/FR(J+1)
      YN=ABS(RC(J+1)-CALCC)
C
C     INITIAL PLACEMENT
      S2=(XN-X0)*(F(LIMIT-1)/F(LIMIT))
      X1=XN-S2
      X2=X0+S2
      FR(J+1)=X1+FR(1)-FS
      RB(J+1)=(X1*EB(J)+FR(1)*RB(1)-FS*SB)/FR(J+1)
      CALL INTERP(M,ARB,ARC,RB(J+1),RC(J+1))
      CALCC=(X1*EC(J)+FR(1)*RC(1)-FS*SC)/FR(J+1)
      Y1=ABS(RC(J+1)-CALCC)
      FR(J+1)=X2+FR(1)-FS
      RB(J+1)=(X2*EB(J)+FR(1)*RB(1)-FS*SB)/FR(J+1)
      CALL INTERP(M,ARB,ARC,RB(J+1),RC(J+1))
      CALCC=(X2*EC(J)+FR(1)*RC(1)-FS*SC)/FR(J+1)
      Y2=ABS(RC(J+1)-CALCC)
C
C     SEARCH
      LLIM=LIMIT-2
      DO 61 NOFIB=1,LLIM
      IF(Y1.GE.Y2) GO TO 60
      XN=X2
      YN=Y2
      X2=X1
      Y2=Y1
      X0=X0
      Y0=Y0
      X1=X0+(XN-X2)
      FR(J+1)=X1+FR(1)-FS
      RB(J+1)=(X1*EB(J)+FR(1)*RB(1)-FS*SB)/FR(J+1)
      CALL INTERP(M,ARB,ARC,RB(J+1),RC(J+1))
      CALCC=(X1*EC(J)+FR(1)*RC(1)-FS*SC)/FR(J+1)
      Y1=ABS(RC(J+1)-CALCC)
      IF(X1.LT.X2) GO TO 61
      XX=X1
      YY=Y1
      X1=X2
      Y1=Y2
      X2=XX
      Y2=YY
      GO TO 61
   60 X0=X1
      Y0=Y1
      X1=X2
      Y1=Y2
      XN=XN
      YN=YN
      X2=XN-(X1-X0)
      FR(J+1)=X2+FR(1)-FS
      RB(J+1)=(X2*EB(J)+FR(1)*RB(1)-FS*SB)/FR(J+1)
      CALL INTERP(M,ARB,ARC,RB(J+1),RC(J+1))
      CALCC=(X2*EC(J)+FR(1)*RC(1)-FS*SC)/FR(J+1)
```

```
      Y2=ABS(RC(J+1)-CALCC)
      IF(X1.LT.X2) GO TO 61
      XX=X1
      YY=Y1
      X1=X2
      Y1=Y2
      X2=XX
      Y2=YY
   61 CONTINUE
C
C
C     STAGE MATERIAL BALANCE
      FE(J)=(X1+X2)/2.0
      FR(J+1)=FE(J)+FR(1)-FS
      RB(J+1)=(FE(J)*EB(J)+FR(1)*RB(1)-FS*SB)/FR(J+1)
      CALL INTERP(M,ARB,ARC,RB(J+1),RC(J+1))
      RA(J+1)=100.0-RB(J+1)-RC(J+1)
C
C     PRINT CONCENTRATIONS AND FLOWS
      FRA(J)=FR(J)*RA(J)
      FRB(J)=FR(J)*RB(J)
      FRC(J)=FR(J)*RC(J)
      FEA(J)=FE(J)*EA(J)
      FEB(J)=FE(J)*EB(J)
      FEC(J)=FE(J)*EC(J)
      F1=FE(J)
      F2=FR(J)
      F3=FEA(J)/100.0
      F4=FEB(J)/100.0
      F5=FEC(J)/100.0
      F6=FRA(J)/100.0
      F7=FRB(J)/100.0
      F8=FRC(J)/100.0
      IF(ENC.LE.EC(J)) GO TO 70
      PRINT 968,RA(J),RB(J),RC(J),EA(J),EB(J),EC(J),F2,F1,F6,F7,F8,F3,
     1    F4,F5
      GO TO 71
   70 F2=FR(J)
      F1=FE(J)
      F6=FR(J)*RA(J)/100.0
      F7=FR(J)*RB(J)/100.0
      F8=FR(J)*RC(J)/100.0
      PRINT 971,RA(J),RB(J),RC(J),EA(J),EB(J),EC(J),F2,F6,F7,F8
   71 IF(ENC.LE.EC(J)) CALL EFFCY(ENC,EC(J-1),EC(J),J)
      IF(ENC.LE.EC(J)) GO TO 100
      IF(J.LE.LIM) GO TO 10
      PRINT 969,LIM
      PRINT 970
C
C
C
  100 CONTINUE
C
C     FORMAT STATEMENTS
  900 FORMAT(3I4)
  901 FORMAT(2F6.2)
```

```
  902 FORMAT(3F6.2)
  903 FORMAT(F6.1,I3)
  904 FORMAT(5F6.3)
  905 FORMAT(3F6.3)
C
  950 FORMAT(43X,47HLIQUID-LIQUID EXTRACTION EFFICIENCY CALCULATION/)
  951 FORMAT(60X,12HSTEADY STATE///)
  952 FORMAT(48X,36HSYSTEM =  WATER - ACETIC ACID - MIBK//)
  953 FORMAT(61X,9HA - WATER)
  954 FORMAT(61X,8HB - MIBK)
  955 FORMAT(61X,15HC - ACETIC ACID//)
  956 FORMAT(51X,8HRUN NO. I3,10X,5HRPM =I4//)
  957 FORMAT(   6X,22X,1HA,19X,1HB,19X,1HC,13X,13HDENSITY-GM/ML,8X,
     1          11HFLOW-ML/MIN/)
  958 FORMAT(13X,2HEN,F16.3,4F20.3)
  959 FORMAT(13X,2HR1,F16.3,4F20.3)
  960 FORMAT(13X,2HS ,F16.3,4F20.3)
  961 FORMAT(13X,2HF ,F16.3,4F20.3/)
  962 FORMAT(57X,17HMATERIAL BALANCES/)
  963 FORMAT(29X,11HTOTAL OUT =F7.3,10X,10HTOTAL IN =F7.3,11X,9HBALANCE
     1=F7.2)
  964 FORMAT(29X,11HHAC OUT   =F7.3,10X,10HHAC IN   =F7.3,11X,9HBALANCE
     1=F7.2//)
  965 FORMAT(51X,32HCALCULATION PROCEEDS FROM BOTTOM///)
  966 FORMAT(17X,26HCONCENTRATIONS-WT PER CENT,40X,12HFLOWS-GM/MIN/)
  967 FORMAT(9X,2HRA,6X,2HRB,6X,2HRC,6X,2HEA,6X,2HEB,6X,2HEC,9X,2HFR,
     1  6X,2HFE,6X,3HFRA,5X,3HFRB,5X,3HFRC,5X,3HFEA,5X,3HFEB,5X,3HFEC//)
  968 FORMAT(5X,6F8.3,3X,8F8.3//)
  969 FORMAT(56X,16HERROR-MORE THAN I3,6HSTAGES///)
  970 FORMAT(1H1)
  971 FORMAT(5X,6F8.3,3X,F8.3,8X,3F8.3//)
C
      STOP
      END



      SUBROUTINE INTERP(JK,X,Y,XA,YA)
      DIMENSION X(30),Y(30)
      YA=0.0
      IF((X(1)-X(2)).GT.0.0) GO TO 804
      DO 805 II=1,JK
      IF((XA-X(II)).LE.0.0) GO TO 806
  805 CONTINUE
  804 DO 809 II=1,JK
      IF((X(II)-XA).LE.0.0) GO TO 806
  809 CONTINUE
  806 IF(II.LE.3) GO TO 807
      IF(II.GE.(JK-2)) GO TO 808
      MM=II-3
      MMM=II+2
      GO TO 810
  807 MM=1
```

```
      MMM=6
      GO TO 810
808   MM=JK-5
      MMM=JK
810   DO 801 I=MM,MMM
      PROD=Y(I)
      DO 800 J=MM,MMM
      IF(J.EQ.I) GO TO 800
      PROD=PROD*(XA-X(J))/(X(I)-X(J))
800   CONTINUE
801   YA=YA+PROD
      RETURN
      END



      SUBROUTINE EFFCY(A,B,C,J)
      COMMON ACTSG
      FRACT=(A-B)/(C-B)
      Z=J-1
      YY=Z+FRACT
      EFF=100.0*YY/ACTSG
      PRINT 802,EFF,YY
      PRINT 803
802   FORMAT(33X,12HEFFICIENCY = F7.3,10X,31HNUMBER OF THEORETICAL STAGE
     1S = F6.3/)
803   FORMAT(1H1)
      RETURN
      END
```

4.2   TRANSIENT MODEL - STEADY STATE CONCENTRATIONS

```
C      TRANSIENT MODEL      RUNGE-KUTTA-GILL                GARY POLLOCK
C
C
       DIMENSION EQXR(30),EQYE(30),X(40),Y(40),V(40),RK(40),EK(40),
      1  RQ(40),EQ(40),WR(40),WE(40),TX(40),TY(40)
       TX=0.0
       TY=0.0
       READ 900,L
       DO 10 J=1,L
       READ 901,EQEC,EQRC
       EQYE(J)=EQEC/(100.0-EQEC)
   10  EQXR(J)=EQRC/(100.0-EQRC)
       READ 900,NDATA
       DO 200 K=1,NDATA
       READ 900,NOSTGE
       M=NOSTGE
       N=M+1
       NN=M+2
       READ 910,VWR,VWE,VV
       STGN=M
       DO 15 I=2,N
       WE(I)=VWE/STGN
       WR(I)=VWR/STGN
   15  V(I)=VV/STGN
       READ 910,DT,TLIM
       READ 910,AKE,F,S
       IF(TLIM.GT.51.0) GO TO 20
       READ 910,XIN,XOUT,YIN,YOUT
       DFX=(XIN-XOUT)/(STGN)
       DFY=(YOUT-YIN)/(STGN)
       X(1)=XIN
       Y(2)=YOUT
       DO 16 J=2,N
       X(J)=X(J-1)-DFX
   16  Y(J+1)=Y(J)-DFY
       Y(N+1)=YIN + 0.00001
       X(N)=XOUT
       GO TO 25
   20  DO 21 I=2,N
       X(I-1)=TX(I-1)
   21  Y(I)=TY(I)
   25  T=0.0
       PRINT 923
       PRINT 924,M
       PRINT 925,V(2),TLIM,AKE
       PRINT 926,WE(2),S
       PRINT 927,WR(2),F
       PRINT 928,XIN,XOUT
       PRINT 929,YOUT,YIN
  100  IF(M.EQ.1) PRINT 911,T,X(1),(Y(I),X(I),I=2,N),Y(NN)
       IF(M.EQ.2) PRINT 912,T,X(1),(Y(I),X(I),I=2,N),Y(NN)
```

```
      IF(M.EQ.3) PRINT 913,T,X(1),(Y(I),X(I),I=2,N),Y(NN)
      IF(M.EQ.4) PRINT 914,T,X(1),(Y(I),X(I),I=2,N),Y(NN)
      IF(M.EQ.5) PRINT 915,T,X(1),(Y(I),X(I),I=2,N),Y(NN)
      IF(M.EQ.6) PRINT 916,T,X(1),(Y(I),X(I),I=2,N),Y(NN)
      IF(M.EQ.7) PRINT 917,T,X(1),(Y(I),X(I),I=2,N),Y(NN)
      IF(M.LT.8) GO TO 30
      IF(M.GE.8) PRINT 918,T
      PRINT 919,X(1),(Y(I),X(I),I=2,N),Y(NN)
   30 CONTINUE
      DO 50 I=2,N
      CALL INTERP(L,EQXR,EQYE,X(I),YY)
      AA=AKE*V(I)*(YY-Y(I))
      RK(I)=DT*(F*X(I-1)-F*X(I)-AA)/WR(I)
      EK(I)=DT*(S*Y(I+1)-S*Y(I)+AA)/WE(I)
      X(I)=X(I)+RK(I)/2.0
      Y(I)=Y(I)+EK(I)/2.0
      RQ(I)=RK(I)
   50 EQ(I)=EK(I)
      DO 51 I=2,N
      CALL INTERP(L,EQXR,EQYE,X(I),YY)
      AA=AKE*V(I)*(YY-Y(I))
      RK(I)=DT*(F*X(I-1)-F*X(I)-AA)/WR(I)
      EK(I)=DT*(S*Y(I+1)-S*Y(I)+AA)/WE(I)
      X(I)=X(I)+(1.0-1.0/SQRT(2.0))*(RK(I)-RQ(I))
      Y(I)=Y(I)+(1.0-1.0/SQRT(2.0))*(EK(I)-EQ(I))
      RQ(I)=(2.0-SQRT(2.0))*RK(I)+(-2.0+3.0/SQRT(2.0))*RQ(I)
   51 EQ(I)=(2.0-SQRT(2.0))*EK(I)+(-2.0+3.0/SQRT(2.0))*EQ(I)
      DO 52 I=2,N
      CALL INTERP(L,EQXR,EQYE,X(I),YY)
      AA=AKE*V(I)*(YY-Y(I))
      RK(I)=DT*(F*X(I-1)-F*X(I)-AA)/WR(I)
      EK(I)=DT*(S*Y(I+1)-S*Y(I)+AA)/WE(I)
      X(I)=X(I)+(1.0+1.0/SQRT(2.0))*(RK(I)-RQ(I))
      Y(I)=Y(I)+(1.0+1.0/SQRT(2.0))*(EK(I)-EQ(I))
      RQ(I)=(2.0+SQRT(2.0))*RK(I)-(2.0+3.0/SQRT(2.0))*RQ(I)
   52 EQ(I)=(2.0+SQRT(2.0))*EK(I)-(2.0+3.0/SQRT(2.0))*EQ(I)
      DO 53 I=2,N
      CALL INTERP(L,EQXR,EQYE,X(I),YY)
      AA=AKE*V(I)*(YY-Y(I))
      RK(I)=DT*(F*X(I-1)-F*X(I)-AA)/WR(I)
      EK(I)=DT*(S*Y(I+1)-S*Y(I)+AA)/WE(I)
      X(I)=X(I)+RK(I)/6.0-RQ(I)/3.0
   53 Y(I)=Y(I)+EK(I)/6.0-EQ(I)/3.0
      T=T+DT
      IF(T.LT.TLIM.AND.TLIM.LT.51.0) GO TO 30
      IF(T.LE.TLIM) GO TO 100
      IF(TLIM.GT.51.0) GO TO 200
      DO 60 I=2,N
      TX(I-1)=X(I-1)
   60 TY(I)=Y(I)
  200 PRINT 920
  900 FORMAT(2I4)
  901 FORMAT(2F6.2)
  910 FORMAT(10F8.4)
```

```
911 FORMAT(10X,F8.2,10X,2(4X,2F14.4))
912 FORMAT(10X,F8.2,8X,3(3X,2F13.4))
913 FORMAT(10X,F8.2,6X,4(3X,2F11.4))
914 FORMAT(7X,F8.2,6X,5(3X,2F9.4))
915 FORMAT(5X,F8.2,6X,6(2X,2F8.4))
916 FORMAT(5X,F7.2,6X,7(2X,2F7.4))
917 FORMAT(1X,F7.2,3X,8(1X,2F7.4))
918 FORMAT(10X,F8.2)
919 FORMAT(24X,F11.4,F9.4,F11.4,F9.4,F11.4,F9.4,F11.4,F9.4,F11.4,F9.4)
920 FORMAT(1H1)
923 FORMAT(35X,51HIDEALLY MIXED NON-EQUILIBRIUM STAGE TRANSIENT MODEL/
   1//)
924 FORMAT(51X,18HNUMBER OF STAGES =,I3//)
925 FORMAT(20X,4HV  =,F7.2,22X,6HTLIM =,F7.2,23X,5HKEA =,F7.3/)
926 FORMAT(20X,4HWE =,F7.2,58X,5HS    =,F7.3/)
927 FORMAT(20X,4HWR =,F7.2,58X,5HF    =,F7.3//)
928 FORMAT(35X,6HXIN  =,F8.4,23X,6HXOUT =,F8.4/)
929 FORMAT(35X,6HYOUT =,F8.4,23X,6HYIN  =,F8.4//)
    STOP
    END



    SUBROUTINE INTERP(JK,X,Y,XA,YA)
    DIMENSION X(30),Y(30)
    YA=0.0
    IF((X(1)-X(2)).GT.0.0) GO TO 804
    DO 805 II=1,JK
    IF((XA-X(II)).LE.0.0) GO TO 806
805 CONTINUE
804 DO 809 II=1,JK
    IF((X(II)-XA).LE.0.0) GO TO 806
809 CONTINUE
806 IF(II.LE.3) GO TO 807
    IF(II.GE.(JK-2)) GO TO 808
    MM=II-3
    MMM=II+2
    GO TO 810
807 MM=1
    MMM=6
    GO TO 810
808 MM=JK-5
    MMM=JK
810 DO 801 I=MM,MMM
    PROD=Y(I)
    DO 800 J=MM,MMM
    IF(J.EQ.I) GO TO 800
    PROD=PROD*(XA-X(J))/(X(I)-X(J))
800 CONTINUE
801 YA=YA+PROD
    RETURN
    END
```

4.3   TRANSIENT MODEL - TRANSIENT RESPONSE


```
C       TRANSIENT  MODEL        RUNGE-KUTTA-GILL                    GARY POLLOCK
C
C
        DIMENSION EQXR(30),EQYE(30),X(40),Y(40),V(40),RK(40),EK(40),
       1  RQ(40),EQ(40),WR(40),WE(40),TX(40),TY(40)
        TX=0.0
        TY=0.0
        READ 900,L
        DO 10 J=1,L
        READ 901,EQEC,EQRC
        EQYE(J)=EQEC/(100.0-EQEC)
   10   EQXR(J)=EQRC/(100.0-EQRC)
        READ 900,NDATA
        DO 200 K=1,NDATA
        READ 900,NOSTGE
        M=NOSTGE
        N=M+1
        NN=M+2
        READ 910,VWR,VWE,VV
        STGN=M
        DO 15 I=2,N
        WE(I)=VWE/STGN
        WR(I)=VWR/STGN
   15   V(I)=VV/STGN
        READ 910,DT,TLIM
        TTLM=TLIM-DT
        DKE=0.056*DT/15.48
        IF(TLIM.GT.51.0) READ 910,F,S
        IF(TLIM.GT.51.0) GO TO 20
        READ 910,AKE,F,S
        READ 910,XIN,XOUT,YIN,YOUT
        DFX=(XIN-XOUT)/(STGN)
        DFY=(YOUT-YIN)/(STGN)
        X(1)=XIN
        Y(2)=YOUT
        DO 16 J=2,N
        X(J)=X(J-1)-DFX
   16   Y(J+1)=Y(J)-DFY
        Y(N+1)=YIN + 0.00001
        X(N)=XOUT
        GO TO 25
   20   DO 21 I=2,N
        X(I-1)=TX(I-1)
   21   Y(I)=TY(I)
   25   T=0.0
        PRINT 923
        PRINT 924,M
        PRINT 925,V(2),TLIM,AKE
        PRINT 926,WE(2),S
        PRINT 927,WR(2),F
```

```
      PRINT 928,XIN,XOUT
      PRINT 929,YOUT,YIN
100   IF(M.EQ.1) PRINT 911,T,X(1),(Y(I),X(I),I=2,N),Y(NN)
      IF(M.EQ.2) PRINT 912,T,X(1),(Y(I),X(I),I=2,N),Y(NN)
      IF(M.EQ.3) PRINT 913,T,X(1),(Y(I),X(I),I=2,N),Y(NN)
      IF(M.EQ.4) PRINT 914,T,X(1),(Y(I),X(I),I=2,N),Y(NN)
      IF(M.EQ.5) PRINT 915,T,X(1),(Y(I),X(I),I=2,N),Y(NN)
      IF(M.EQ.6) PRINT 916,T,AKE,X(1),(Y(I),X(I),I=2,N),Y(NN)
      IF(M.EQ.7) PRINT 917,T,X(1),(Y(I),X(I),I=2,N),Y(NN)
      IF(M.LT.8) GO TO 30
      IF(M.GE.8) PRINT 918,T
      PRINT 919,X(1),(Y(I),X(I),I=2,N),Y(NN)
30    CONTINUE
      DO 50 I=2,N
      CALL INTERP(L,EQXR,EQYE,X(I),YY)
      AA=AKE*V(I)*(YY-Y(I))
      RK(I)=DT*(F*X(I-1)-F*X(I)-AA)/WR(I)
      EK(I)=DT*(S*Y(I+1)-S*Y(I)+AA)/WE(I)
      X(I)=X(I)+RK(I)/2.0
      Y(I)=Y(I)+EK(I)/2.0
      RQ(I)=RK(I)
50    EQ(I)=EK(I)
      DO 51 I=2,N
      CALL INTERP(L,EQXR,EQYE,X(I),YY)
      AA=AKE*V(I)*(YY-Y(I))
      RK(I)=DT*(F*X(I-1)-F*X(I)-AA)/WR(I)
      EK(I)=DT*(S*Y(I+1)-S*Y(I)+AA)/WE(I)
      X(I)=X(I)+(1.0-1.0/SQRT(2.0))*(RK(I)-RQ(I))
      Y(I)=Y(I)+(1.0-1.0/SQRT(2.0))*(EK(I)-EQ(I))
      RQ(I)=(2.0-SQRT(2.0))*RK(I)+(-2.0+3.0/SQRT(2.0))*RQ(I)
51    EQ(I)=(2.0-SQRT(2.0))*EK(I)+(-2.0+3.0/SQRT(2.0))*EQ(I)
      DO 52 I=2,N
      CALL INTERP(L,EQXR,EQYE,X(I),YY)
      AA=AKE*V(I)*(YY-Y(I))
      RK(I)=DT*(F*X(I-1)-F*X(I)-AA)/WR(I)
      EK(I)=DT*(S*Y(I+1)-S*Y(I)+AA)/WE(I)
      X(I)=X(I)+(1.0+1.0/SQRT(2.0))*(RK(I)-RQ(I))
      Y(I)=Y(I)+(1.0+1.0/SQRT(2.0))*(EK(I)-EQ(I))
      RQ(I)=(2.0+SQRT(2.0))*RK(I)-(2.0+3.0/SQRT(2.0))*RQ(I)
52    EQ(I)=(2.0+SQRT(2.0))*EK(I)-(2.0+3.0/SQRT(2.0))*EQ(I)
      DO 53 I=2,N
      CALL INTERP(L,EQXR,EQYE,X(I),YY)
      AA=AKE*V(I)*(YY-Y(I))
      RK(I)=DT*(F*X(I-1)-F*X(I)-AA)/WR(I)
      EK(I)=DT*(S*Y(I+1)-S*Y(I)+AA)/WE(I)
      X(I)=X(I)+RK(I)/6.0-RQ(I)/3.0
53    Y(I)=Y(I)+EK(I)/6.0-EQ(I)/3.0
      IF(TLIM.GT.51.0.AND.AKE.LT.0.212)   AKE=AKE+DKE
      T=T+DT
      IF(T.LT.TTLM.AND.TLIM.LT.51.0)  GO TO 30
      IF(T.LE.TLIM) GO TO 100
      IF(TLIM.GT.51.0) GO TO 200
      DO 60 I=2,N
```

```
      TX(I-1)=X(I-1)
   60 TY(I)=Y(I)
  200 PRINT 920
  900 FORMAT(2I4)
  901 FORMAT(2F6.2)
  910 FORMAT(10F8.4)
  911 FORMAT(10X,F8.2,10X,2(4X,2F14.4))
  912 FORMAT(10X,F8.2,8X,3(3X,2F13.4))
  913 FORMAT(10X,F8.2,6X,4(3X,2F11.4))
  914 FORMAT(7X,F8.2,6X,5(3X,2F9.4))
  915 FORMAT(5X,F8.2,6X,6(2X,2F8.4))
  916 FORMAT(1X,F7.2,2X,F5.3,5X,7(2X,2F7.4))
  917 FORMAT(1X,F7.2,3X,8(1X,2F7.4))
  918 FORMAT(10X,F8.2)
  919 FORMAT(24X,F11.4,F9.4,F11.4,F9.4,F11.4,F9.4,F11.4,F9.4,F11.4,F9.4)
  920 FORMAT(1H1)
  923 FORMAT(35X,51HIDEALLY MIXED NON-EQUILIBRIUM STAGE TRANSIENT MODEL/
     1//)
  924 FORMAT(51X,18HNUMBER OF STAGES =,I3//)
  925 FORMAT(20X,4HV  =,F7.2,22X,6HTLIM =,F7.2,23X,5HKEA =,F7.3/)
  926 FORMAT(20X,4HWE =,F7.2,58X,5HS   =,F7.3/)
  927 FORMAT(20X,4HWR =,F7.2,58X,5HF   =,F7.3//)
  928 FORMAT(35X,6HXIN  =,F8.4,23X,6HXOUT =,F8.4/)
  929 FORMAT(35X,6HYOUT =,F8.4,23X,6HYIN  =,F8.4//)
      STOP
      END



      SUBROUTINE INTERP(JK,X,Y,XA,YA)
      DIMENSION X(30),Y(30)
      YA=0.0
      IF((X(1)-X(2)).GT.0.0) GO TO 804
      DO 805 II=1,JK
      IF((XA-X(II)).LE.0.0) GO TO 806
  805 CONTINUE
  804 DO 809 II=1,JK
      IF((X(II)-XA).LE.0.0) GO TO 806
  809 CONTINUE
  806 IF(II.LE.3) GO TO 807
      IF(II.GE.(JK-2)) GO TO 808
      MM=II-3
      MMM=II+2
      GO TO 810
  807 MM=1
      MMM=6
      GO TO 810
  808 MM=JK-5
      MMM=JK
  810 DO 801 I=MM,MMM
      PROD=Y(I)
      DO 800 J=MM,MMM
```

```
      IF(J.EQ.I) GO TO 800
      PROD=PROD*(XA-X(J))/(X(I)-X(J))
800   CONTINUE
801   YA=YA+PROD
      RETURN
      END
```